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Workshop on Novel States and Phase Transitions in Highly Correlated Matter

12 - 23 July 2004

Magnetically controllable ferroelectricity in perovskite rare-earth manganites

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Magnetically controllable ferroelectricity in perovskite rare-earth manganites

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S. Ishihara (Tohoku Univ.) Mean-Field Theory

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Multiferroics ⇒ Materials which exhibit two or all three ferroic orders

ferro-magnetic, ferro-electric, ferroelastic

↘ ↙

Magnetoelectric multiferroics

Magnetization ⟺ Electric polarization

coupling

Magneto-Electric (ME) effect ⇒ Induction of Polarization / Magnetization by Magnetic fields / Electric fields

Early history of the ME effect [from "The electrodynamics of magneto-electric media" by T. H. O'Dell]

Researcher [year]	work
P. Curie [1894]	First proposal of the effect on symmetry grounds
Piccard [1924]	Suggests the impossibility of the effect on symmetry grounds.
Debye [1926]	Suggests the effect is impossible.
Van Vleck [1932]	Devotes a section of his book to the reason why no ME effect can exist.
Landau & Lifshitz [1957]	Shows that the ME effect should exist in magnetic crystals.
Dyaloshinskii [1959]	Shows that the AF Cr_2O_3 has a magnetic symmetry which allows the effect.
Astronov [1960]	First successful observation of the effect in a Cr_2O_3 crystal.

Free energy with the variant electric (E) & magnetic (H) fields

$$F = -\sum_n a_n E^n - \sum_n b_n H^n - \sum_{m,n} c_{m,n} E^m H^n$$

polarization: $\vec{P} = -\partial F / \partial \vec{E}$

magnetization: $\vec{M} = -\partial F / \partial \vec{H}$

ME-coupling term

Linear ME effect

$$\vec{P} = -\partial F / \partial \vec{E} \rightarrow P_i = \sum_{j=1}^{3} \alpha_{ij} H_i$$

$$\vec{M} = -\partial F / \partial \vec{H} \rightarrow M_i = \sum_{j=1}^{3} \alpha_{ij} E_i$$

Perovskite Rare-earth manganites, *R*MnO_3

(parent compounds of CMR manganites)

↓

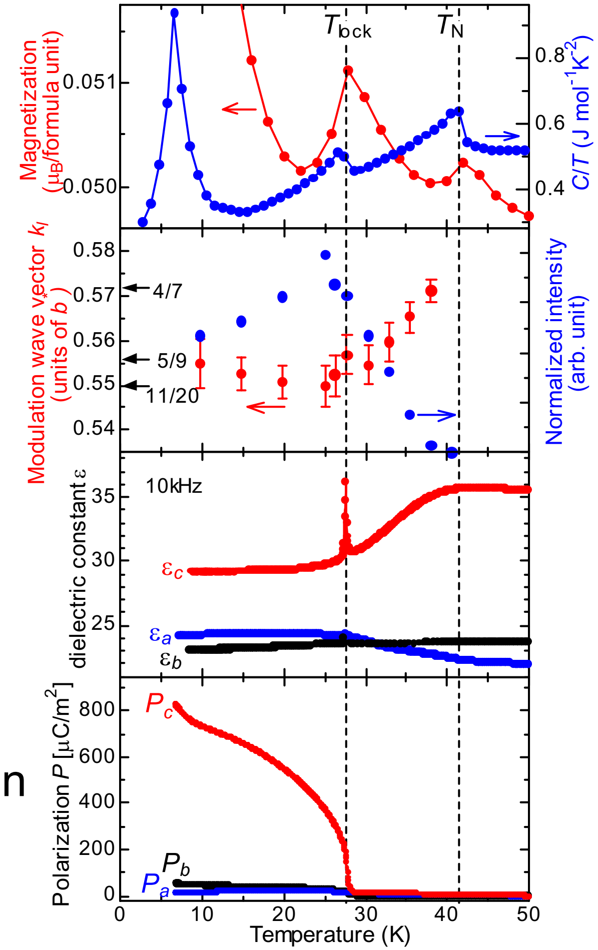
Magnetic ferroelectrics

(orbital order, competing magnetic interactions,
commensurate-incommensurate transition,
magnetoelastic coupling, etc.)

Outline of this talk

1. *Magnetic phase diagram of RMnO_3*
   Origin of their complex magnetic structures
2. *Incommensurate lattice modulation*
   Close relation between lattice and magnetic modulation
3. *Dielectric properties*
   Appearance of ferroelectricity
4. *Magnetic control of ferroelectric polarization*
   Giant magnetoelectric & giant magnetocapacitance effects

$TbMnO_3$



T. Kimura et al.
Nature 426, 55 (2003)

T. Goto, T. Kimura et al.
PRL 92, 257201 (2004)

RMnO$_3$

- Orbital ordering

  $3x^2$-r^2/$3y^2$-r^2

  Anisotropic super exchange
  - Strong FM between e_g orbitals within the *ab* plane
  - Weak AF between t_{2g} orbitals along the *c* axis

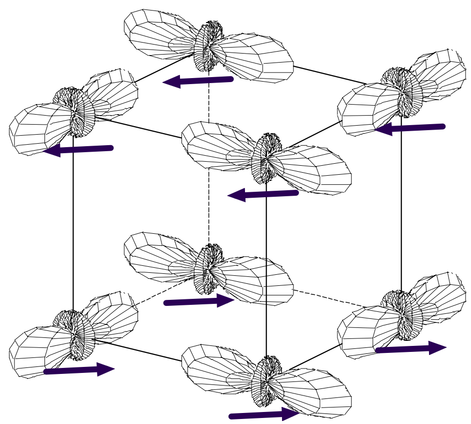
  ⇒ A-type AF
- Ionic radius of *R*: r_R; Mn-O-Mn angle: ϕ

  La, Pr, Nd, Sm, Eu, Gd, Tb, Tb, Dy, Ho

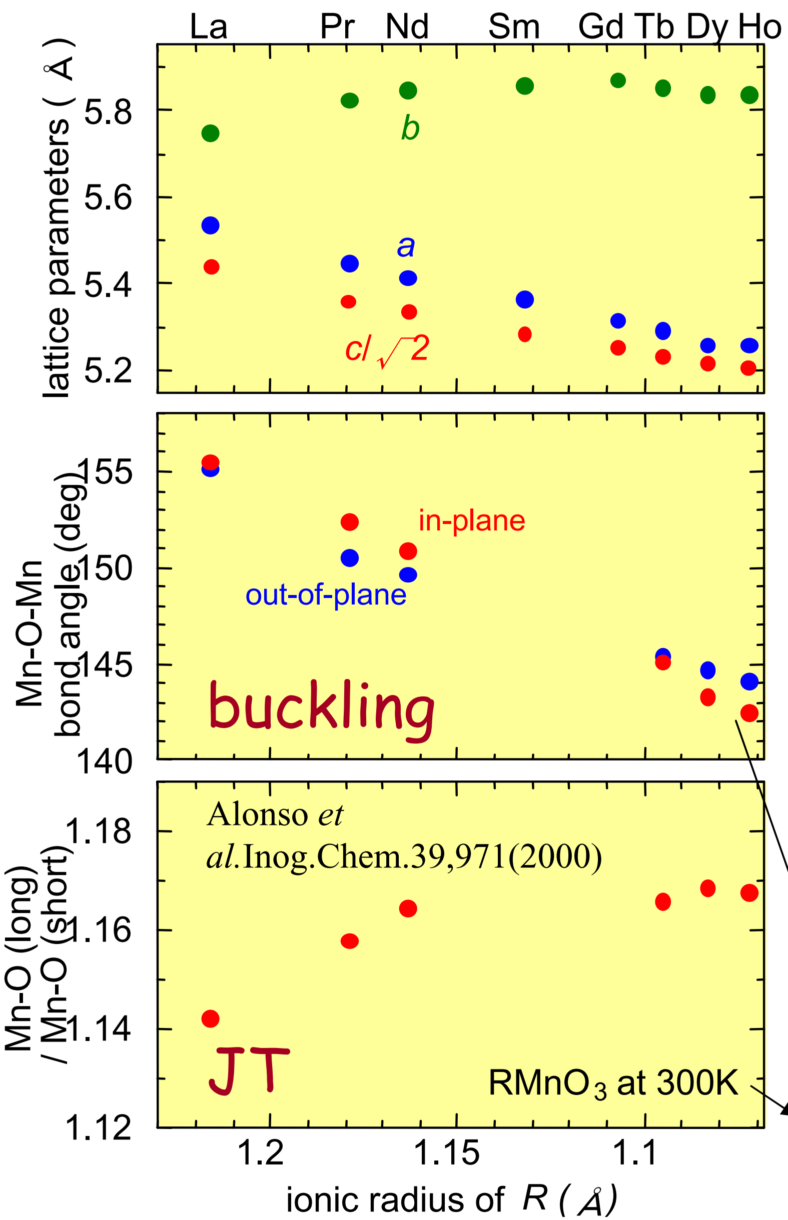
  Large ← r_R → Small

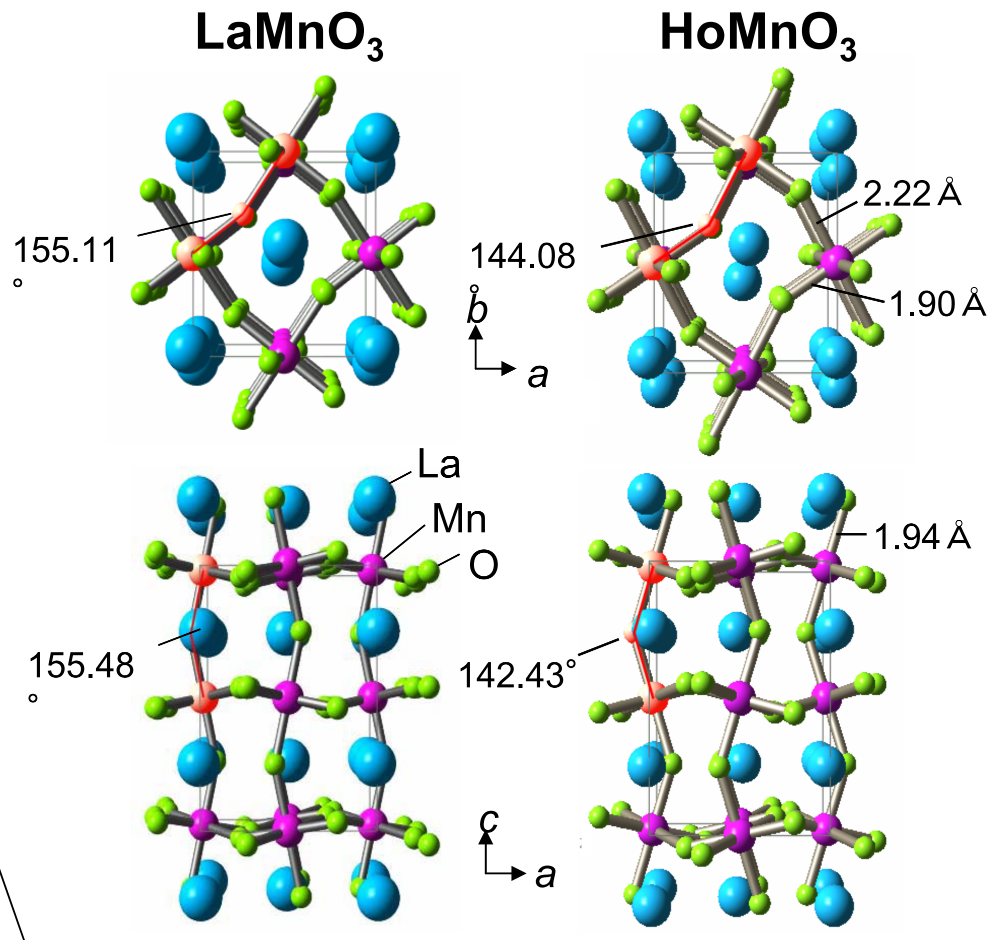
  Large ← ϕ → Small

LaMnO$_3$ etc.



Change of lattice distortion in *R*MnO_3 (all of them are *Pbnm* orthorhombic)



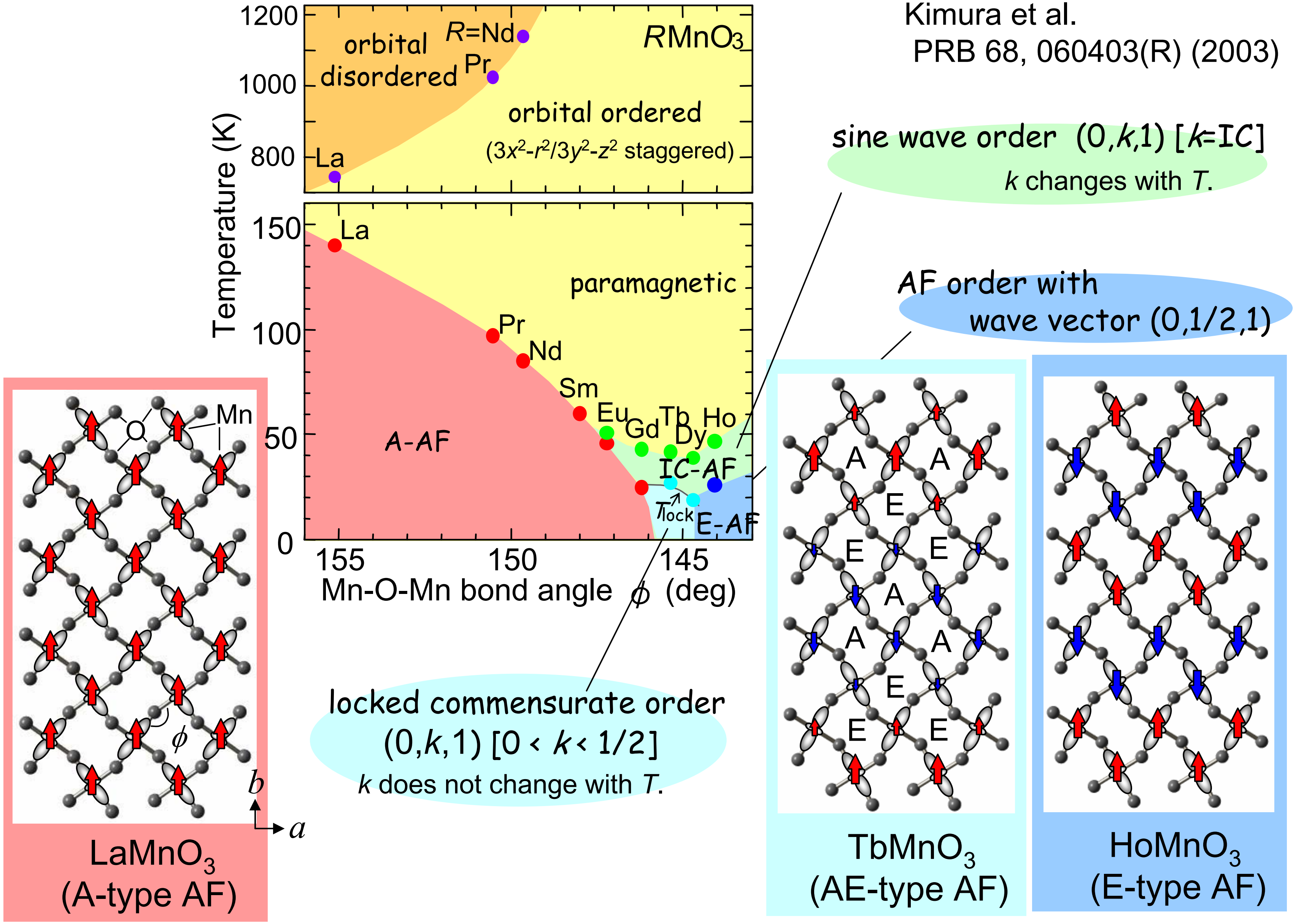


With decrease of ionic radius of *R*

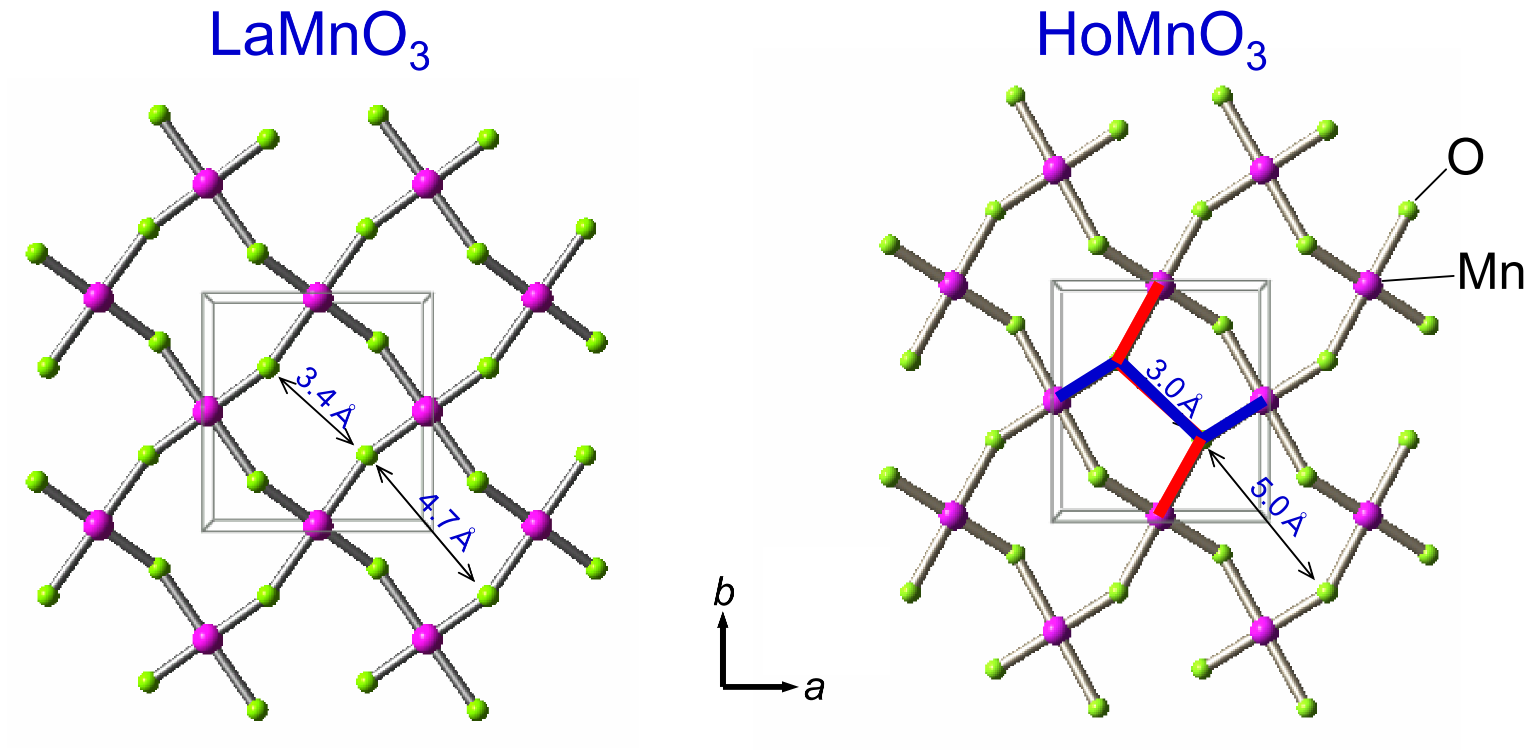
1. Mn-O-Mn bond angle drastically decreases.
2. JT-distortion slightly increases.

Evolution of spin structure against Mn-O-Mn bond angle in $RMnO_3$

Kimura et al.
PRB 68, 060403(R) (2003)



What does $GdFeO_3$-type distortion change?



With increasing the $GdFeO_3$-type distortion, the distance between O sites decreases.

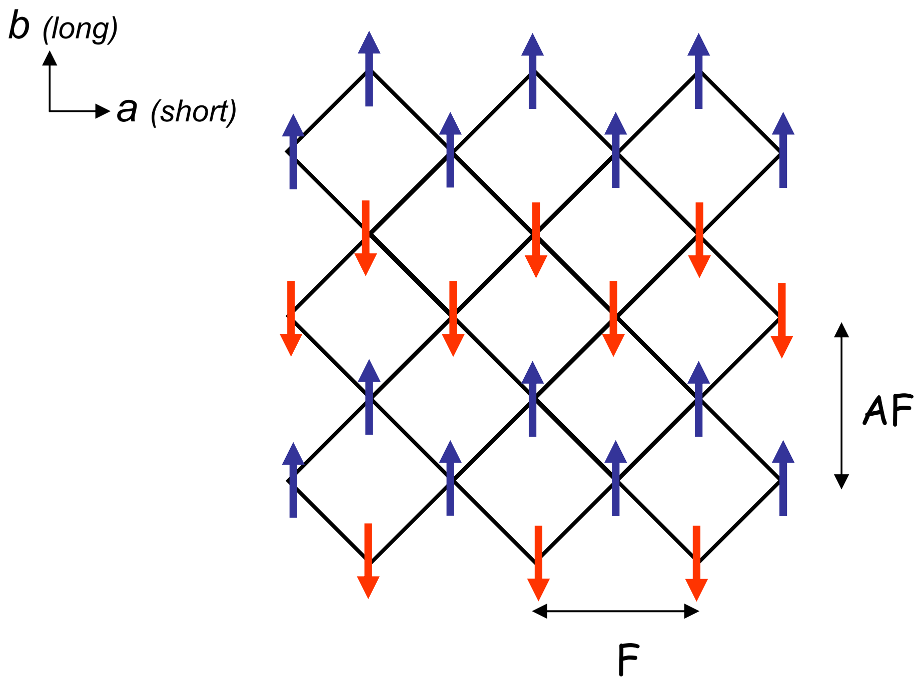
⇓

Interaction between next-nearest neighboring Mn sites should increases.

Munoz et al, Inorg. Chem. 40, 1020 (2001)

Consideration of E-type AF ordered structure

E-type AF order



antiferromagnetic coupling
along the long *b*-axis

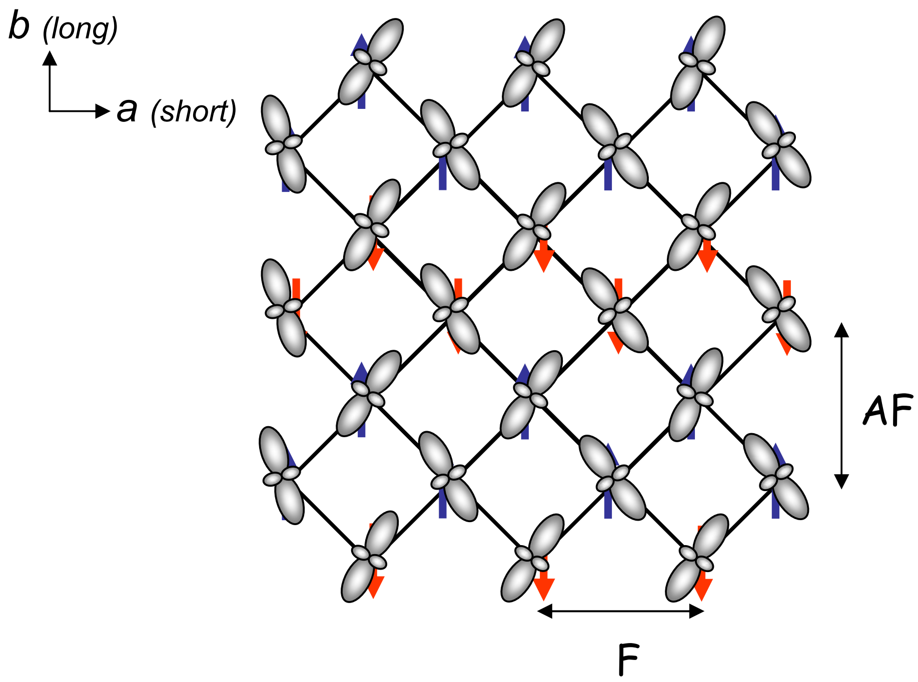
ferromagnetic coupling
along the short *a*-axis

Anisotrpic magnetic coupling
between the a- and b-axes

Why the E-type AF order (anisotropic mangnetic interaction)
appears with decreasing the ionic radius of A-site?

Why the magnetic coupling becomes anisotropic between the directions of the a- and b-axes?

E-type AF order



antiferromagnetic coupling along the long *b*-axis

ferromagnetic coupling along the short *a*-axis

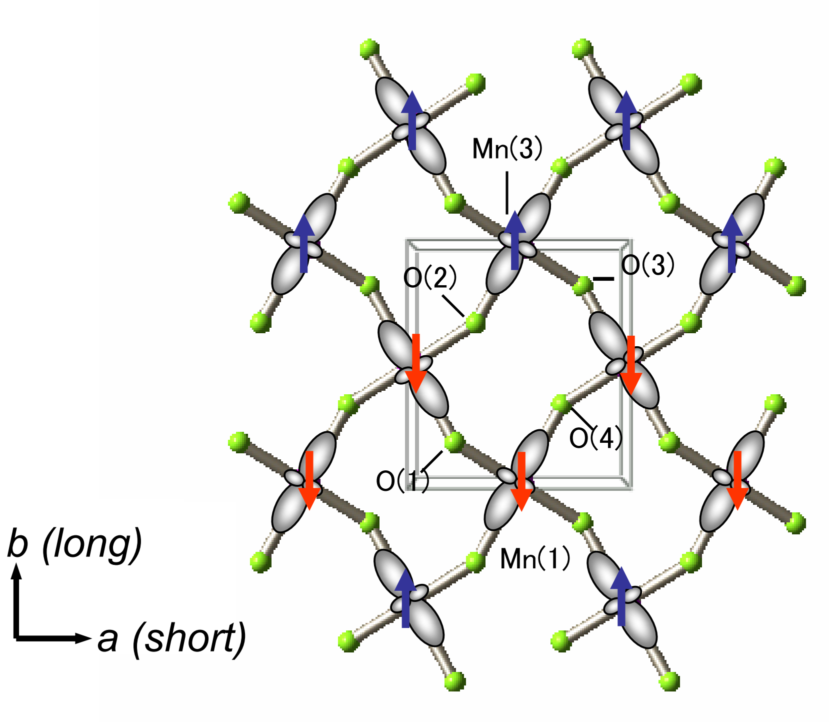
⇩

Anisotrpic magnetic coupling between the a- and b-axes

Effect of orbital ordering

Effect of orbital ordering in distorted $RMnO_3$

E-type AF order



Staggered-type of orbital ordering may cause the anisotropic magnetic interaction between the *a*- and *b*-axes.

Model of distorted $RMnO_3$ system (with Sumio Ishihara)

Model Hamiltonian ⇨ spin-orbit Hamiltonian

[known to describe the orbitally degenerate e_g^1 system (e.g. manganites)

$$H = H_J + H_H + H_{AF}$$

where H_J; main term, exchange interaction between intersite e_g spin and orbital

$$H_J = \Sigma_m J_m \Sigma_{<ij>}(a_m \vec{S}_i \cdot \vec{S}_j + b_m) h_m(\vec{T}_i \cdot \vec{T}_j)$$

SE interaction; Spin operator for e_g electrons; Pseudospin operator for orbital part

H_H; Hund coupling between e_g & t_{2g} spins

H_{AF}; AF SE interaction between NN t_{2g} spins

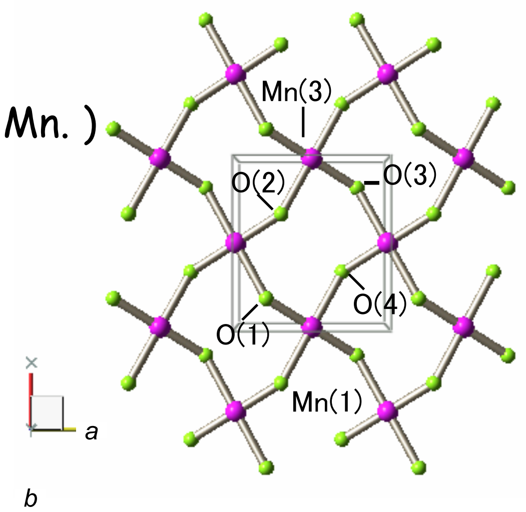
Considering 2D square lattice consisting of Mn ions.
(effect of O ions are included in transfer matrices between Mn.)

⇩

transfer integral between NN Mn ions ~ t_{pd}^2/Δ

NNN Mn ions ~ $t_{pd}^2 t_{pp}/\Delta$

All possible transfer paths are considered.
[Mn(1) - {O(1),O(4)} - {O(2),O(3)} - Mn(3)]



In each O sites, the possible 2p orbitals are summed up.

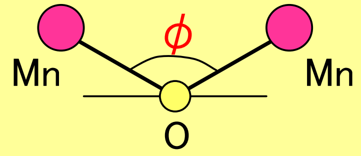
Results of Mean field theory

Controlled parameters

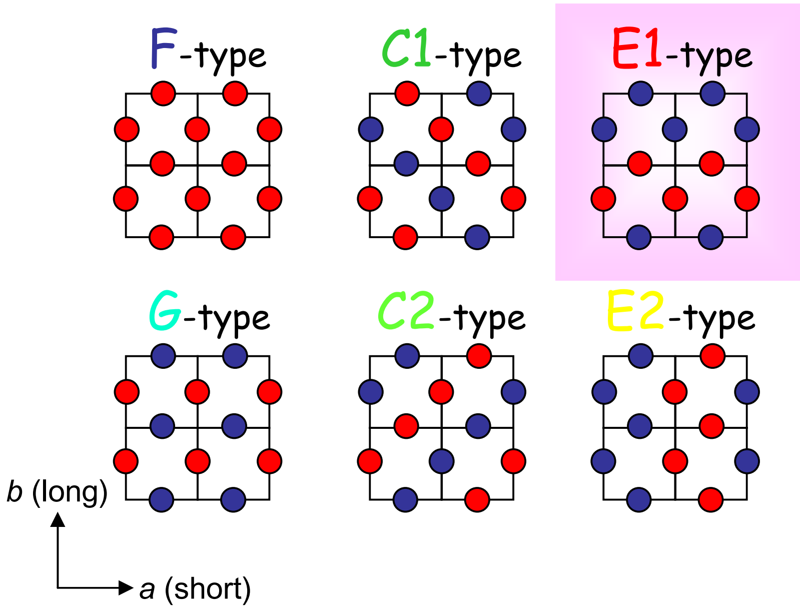
1. θ ⇒ orbital angle in the two orbital sublattices.

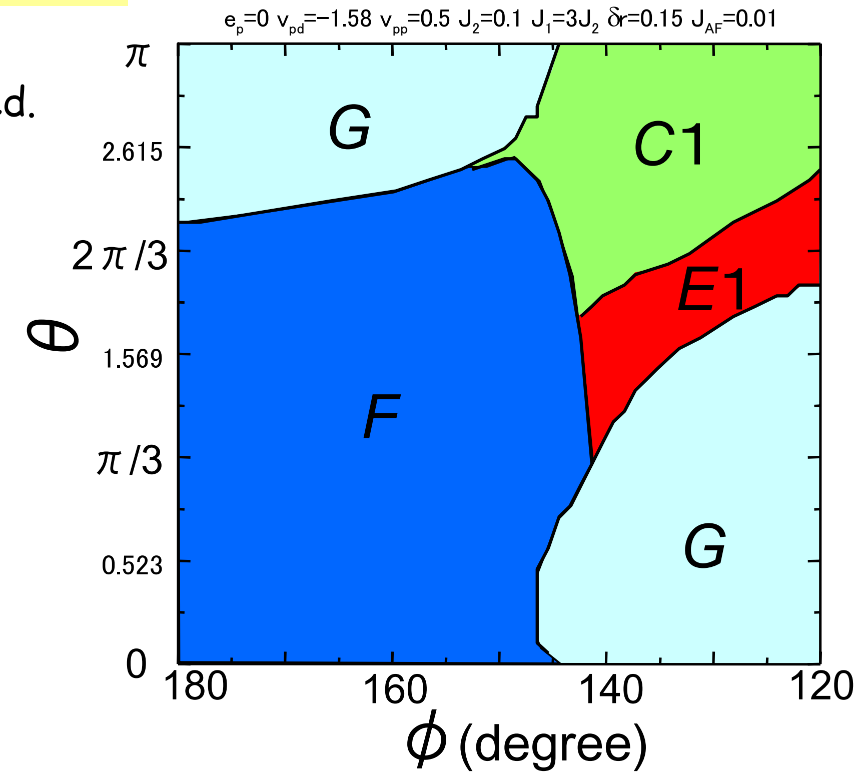
θ	orbital state
0	uniform $d3z^2-r^2$
$\pi/3$	staggered dy^2-z^2/ dz^2-x^2
$2\pi/3$	staggered $d3x^2-r^2$/ $d3y^2-r^2$
π	uniform dx^2-y^2

2. ϕ ⇒Mn−O−Mn bond angle

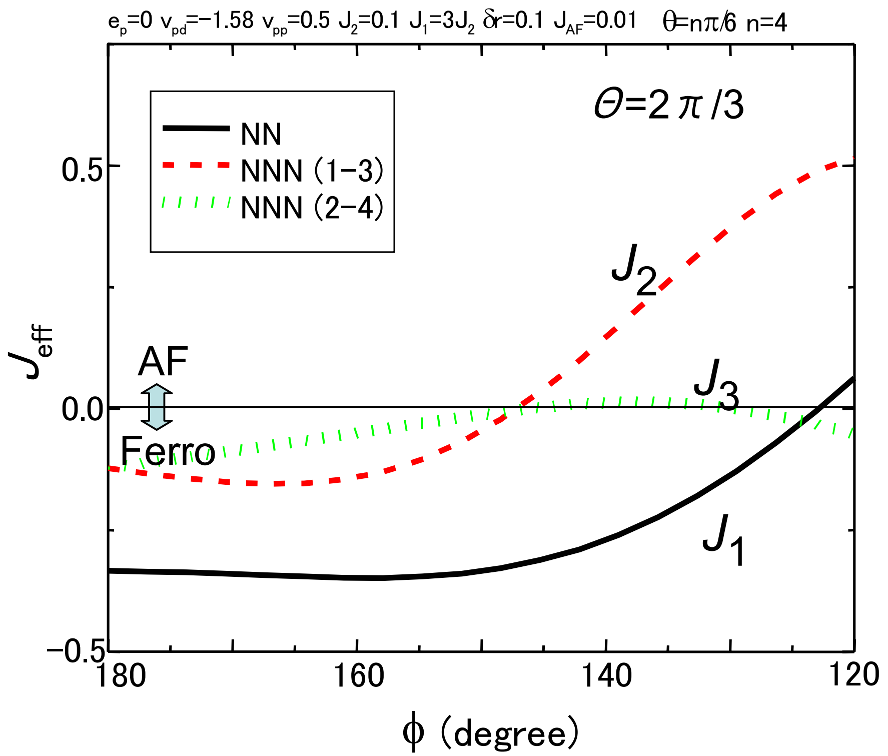


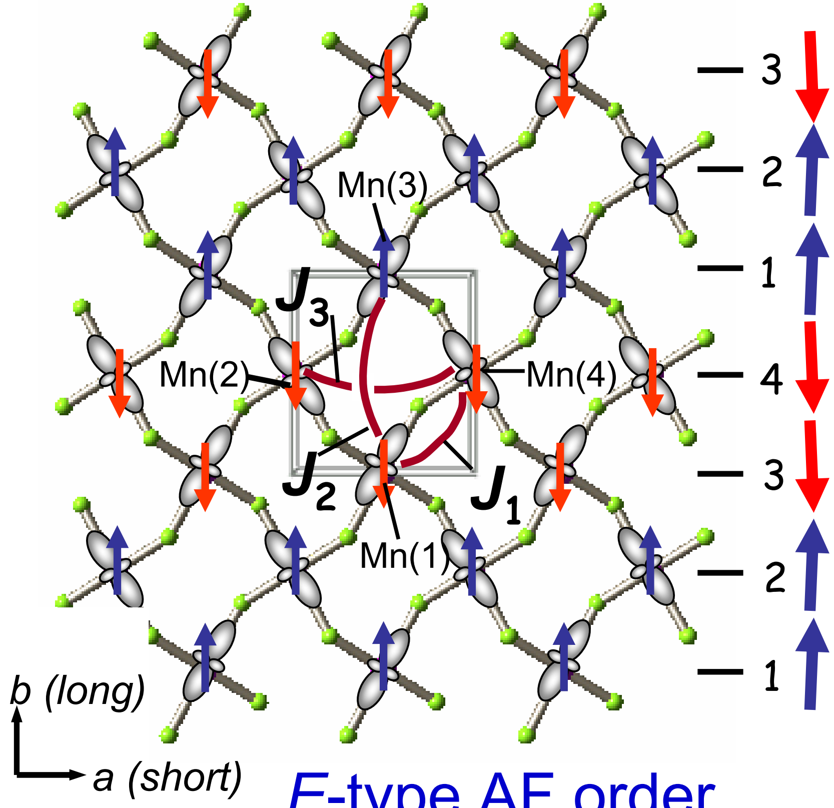
Energies of 6 spin-ordered states are compared.





Origin of complex spin structure -competition between NN and NNN interactions -





E-type AF order

Appearance of E-type AF ordering in distorted $RMnO_3$ may be due to combination of

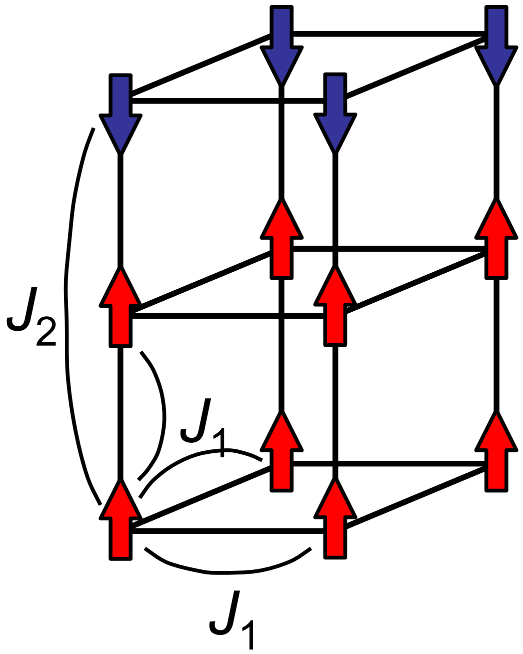
1. staggered-type of Orbital Ordering
2. Competition between FM Nearest-Neighbor and AF Next-Nearest-Neighbor interactions

c.f. Axial Next-Nearset-Neighbor Ising model
Devil's flower [P. Bak, Rep. Prog. Phys. 45, 587 (1982)]

T. Kimura, S. Ishihara et al.
PRB 68, 060403(R) (2003)

ANNNI model (Axial Next-Nearest-Neighbor Ising model)

P. Bak and J. von Boehm, PRB 21, 5297 (1980)

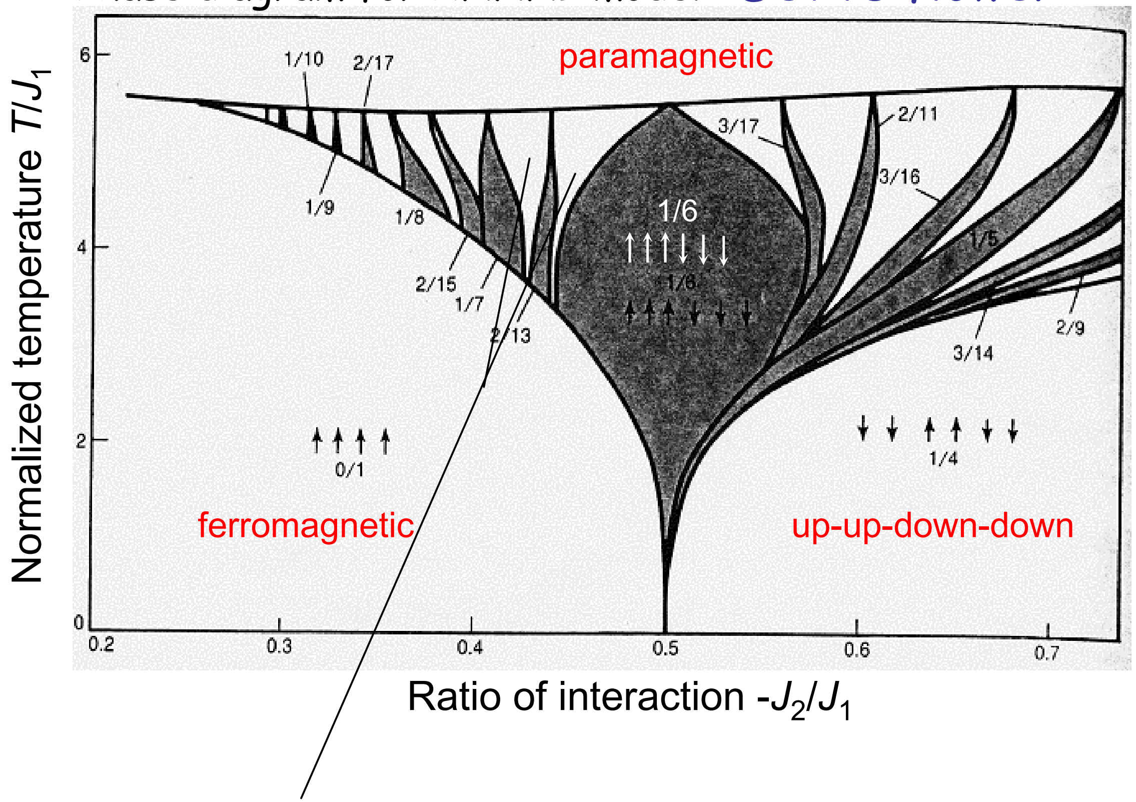


$$\mathcal{H} = -\sum_{<ij>} J_{ij} S_i S_j$$

$J_1>0$ ferro

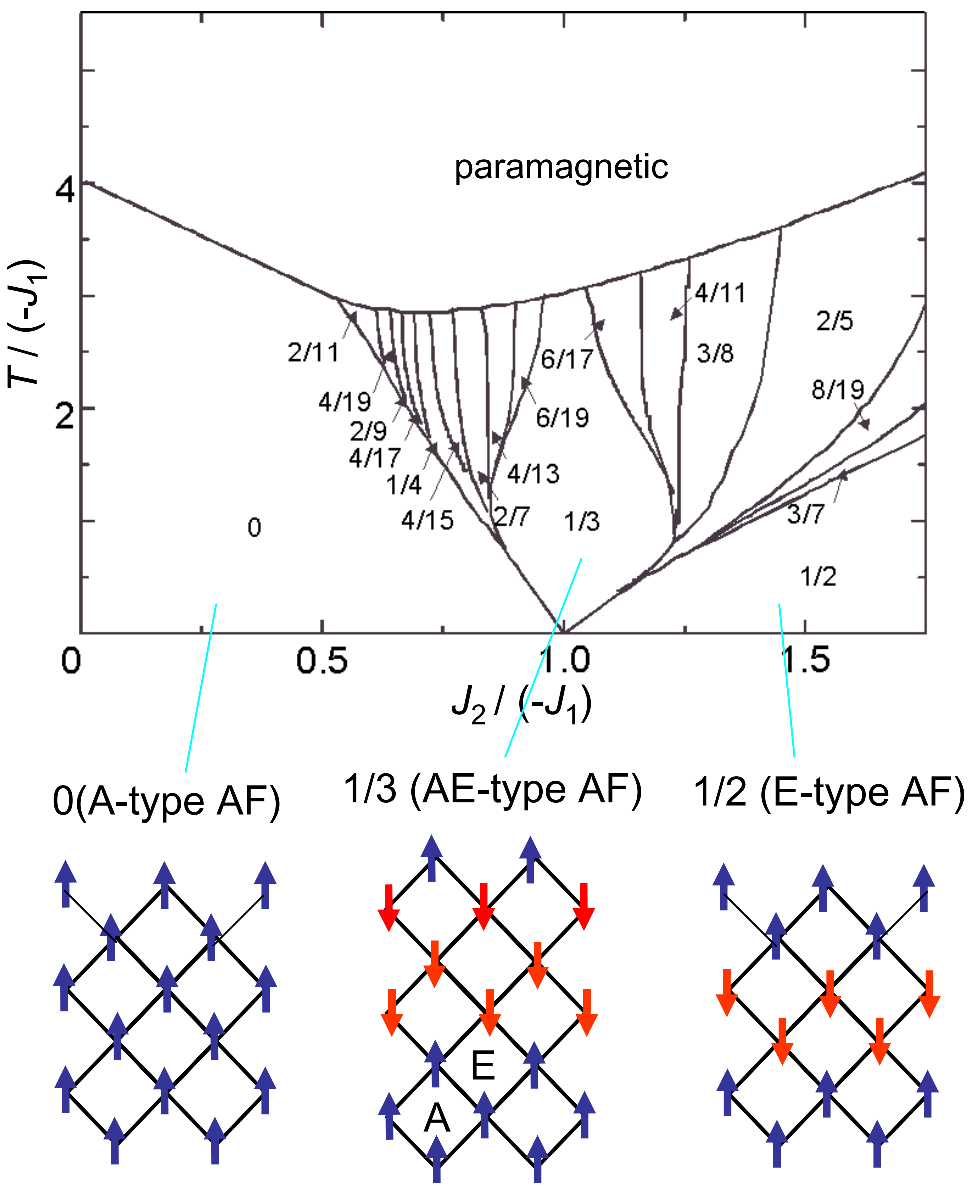
$J_2<0$ AF

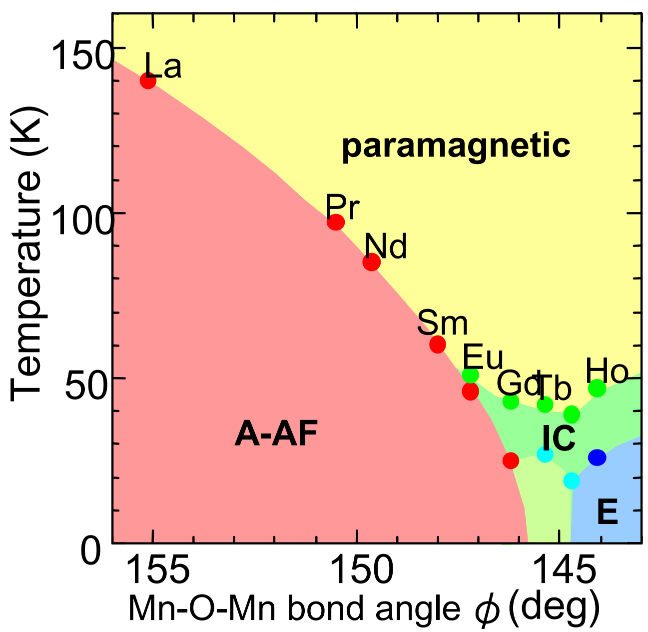
Phase diagram for ANNNI model "Devil's flower"



These areas contain yet more leaves, representing infinities of periodic phases with incommensurate phases between.

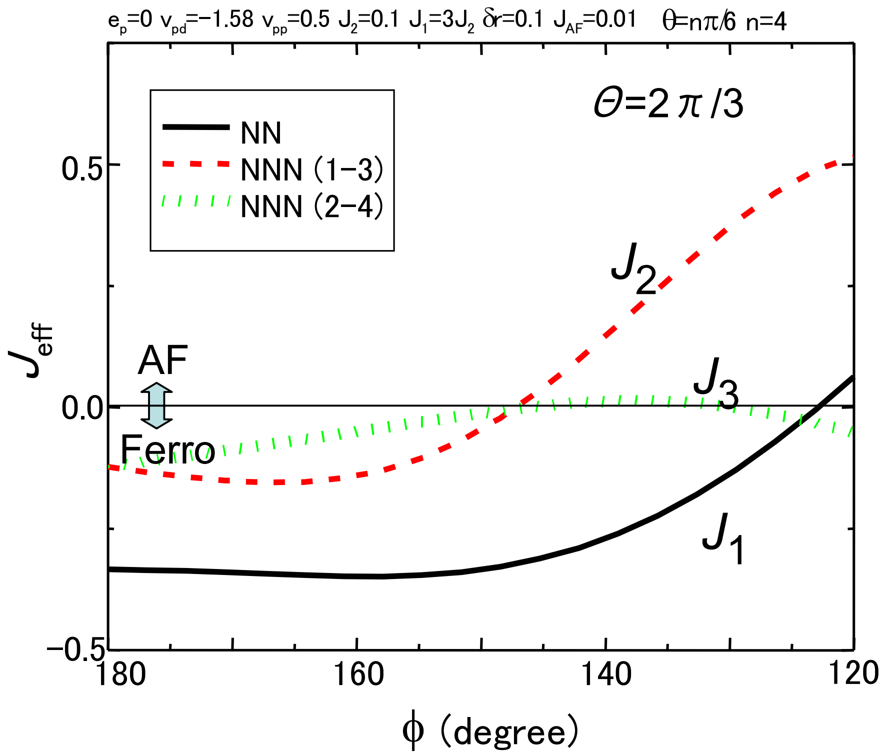
Calculated magnetic phase diagram of 2D J_1-J_2 Ising model

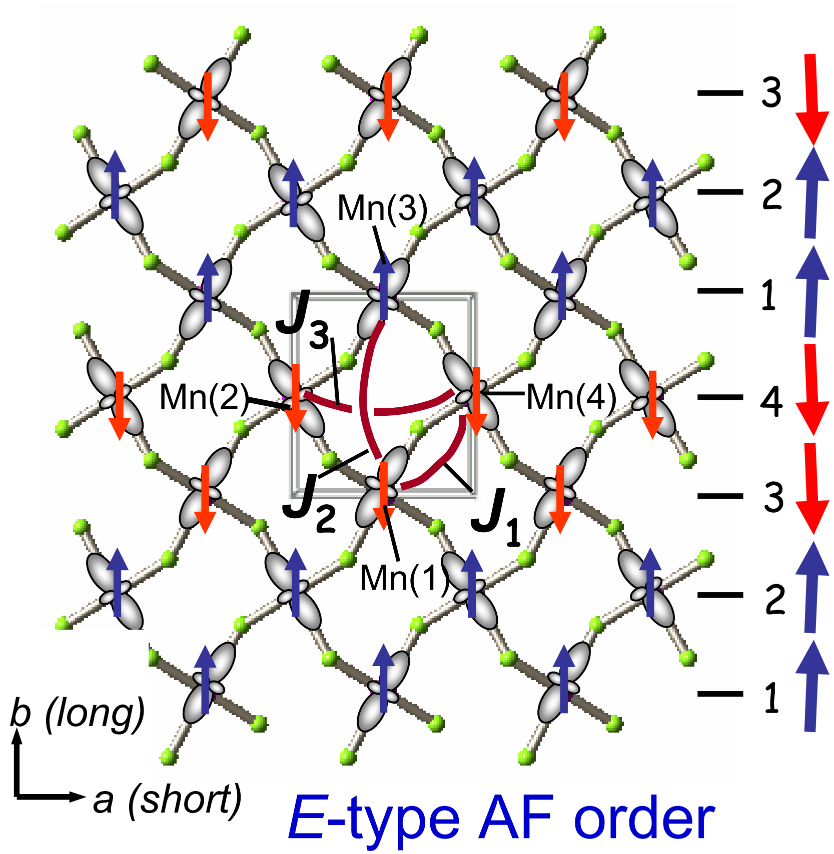




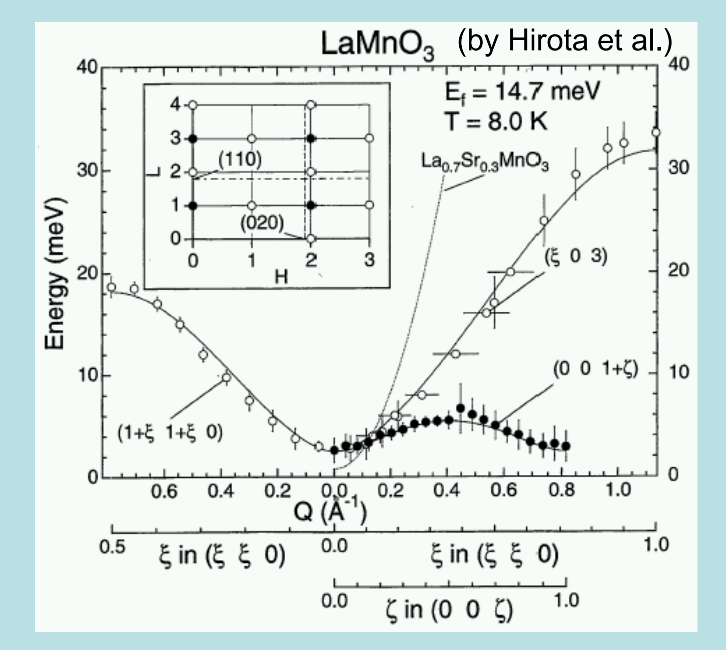
Calculated results qualitatively
explain the experimental results.

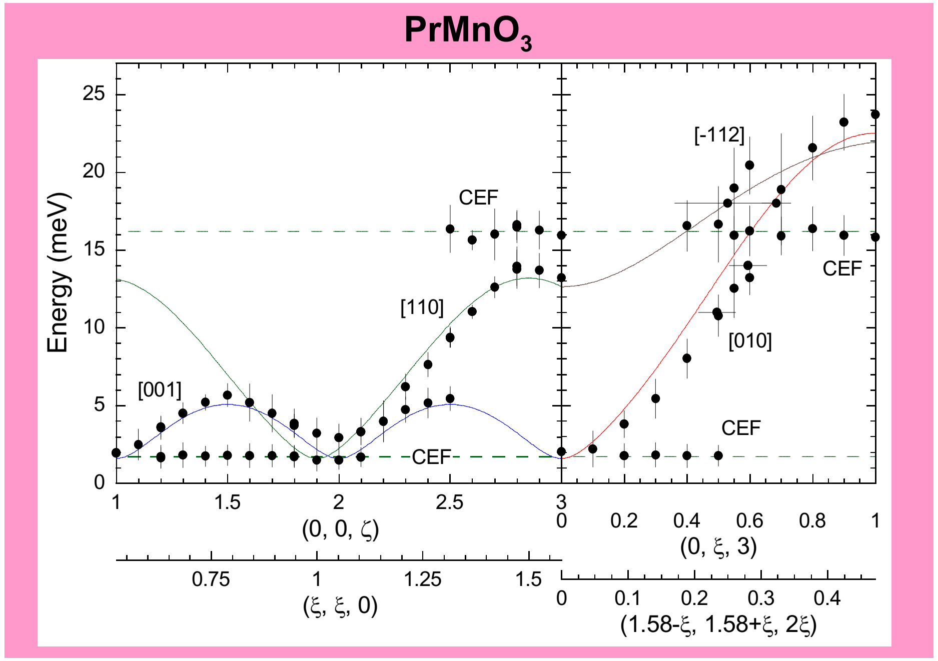
Experimental confirmation of Mn-O-Mn bond angle dependence of exchange interaction

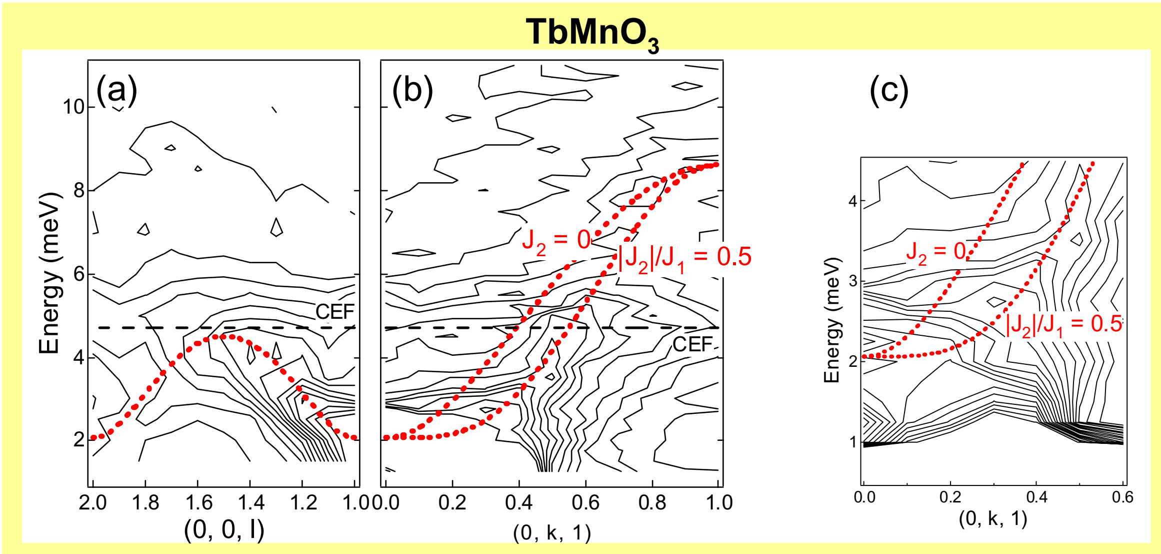




Dispersion relation in $RMnO_3$ (R=La, Pr, & Tb) obtained by inelastic neutron scattering







Fit by the Heisenberg model for an A-type antiferromagnet

*In $LaMnO_3$, $PrMnO_3$ only exchanges between the NN sites are considered.

*In $TbMnO_3$ the NNN exchange are also considered.

		LaMnO$_3$(*)	PrMnO$_3$	TbMnO$_3$
$\perp c$	$8J_1S$(meV)	13.36(18)	9.0(3)	~2.5
	J_2			~–0.5J_1
$\parallel c$	$4J'S$(meV)	–4.84(22)	–4.8(5)	~–4
	$g\mu_B H_A$(meV)	0.61(11)	0.3(2)	~0.5

(*) K. Hirota *et al.*, J. Phys. Soc. Jpn. **65**, 3736 (1996)

$\parallel c$

– *J* is independent of *R*

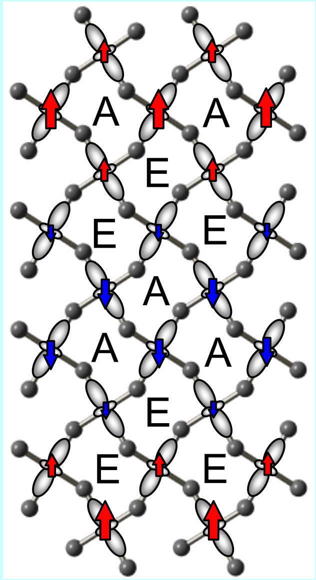
$\perp c$

– *J* is drastically decreases as a function of *R*.
– Magnetic excitations in TbMnO$_3$ are well reproduced with a finite J_2 for $q > q_{IC}$.

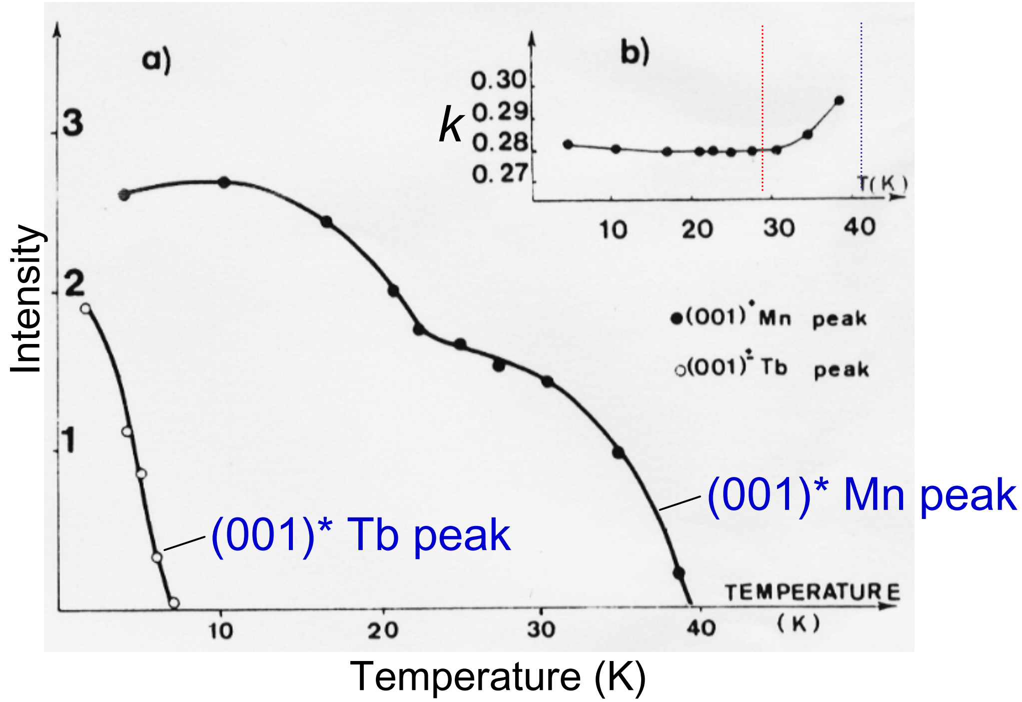
➡ Consistent to the "orbital ordering + GdFeO$_3$ distortion" model

$TbMnO_3$

Neutron diffraction by Quezel et al. [Physica B 86-88, 916 (1977)]
(Kajimoto et al. PRB 70, 012401 (2004))



$TbMnO_3$
(AE-type AF)



*Incommensurate spin ordering with the wave vector of $(0,k,1)$ T_N~40K

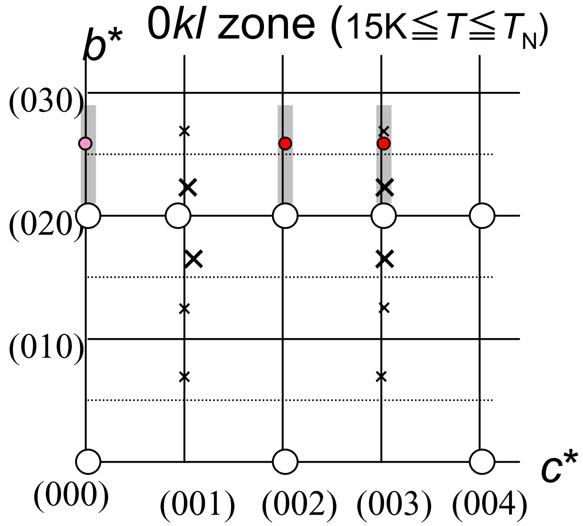
*The wave vector is locked in to k=0.28 below T_{lock}~27K

X-ray scattering measurements of *R*MnO_3

@BL4C PF-KEK, Tsukuba

Search for magnetic Bragg scattering to determine magnetic structure

$TbMnO_3$



○ fundamental Bragg (*Pbnm*)

× spin (*A*) strong; below T_N

× spin (*G*) weak; only below 20K

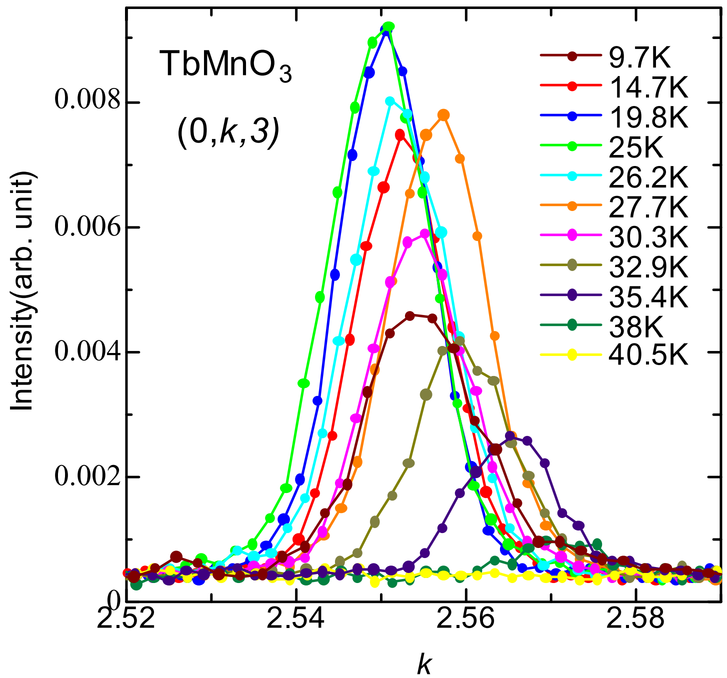
by Quezel et al., Physica B 86-88, 916 (1977)

● superlattice below T_n; strong

● superlattice below T_n; weak

scanned line at this expriment

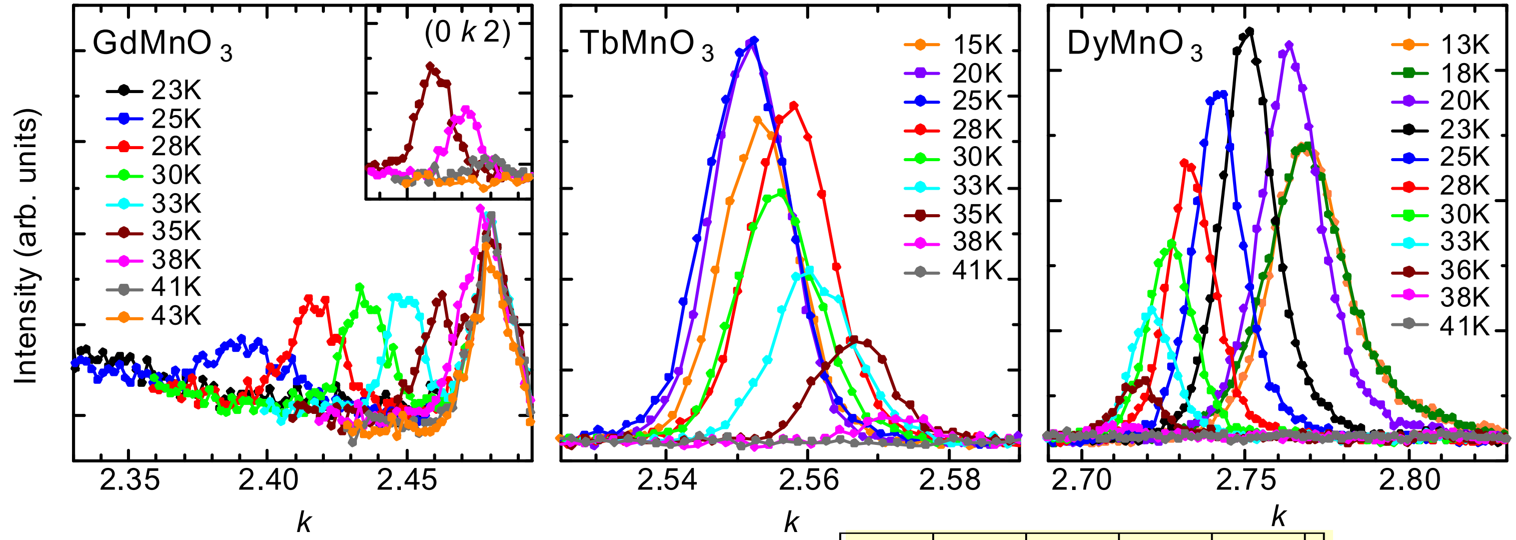
Appearance of structural modulation below T_N



wave vector of newly observed superlattice

⇒ ***q***=(0,~0.55,0)

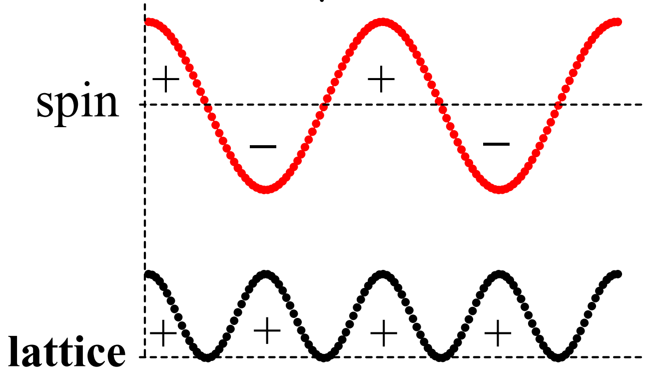
Superlattice reflections due to lattice modulation with wave vector of (0 $k_{lattice}$ 0)

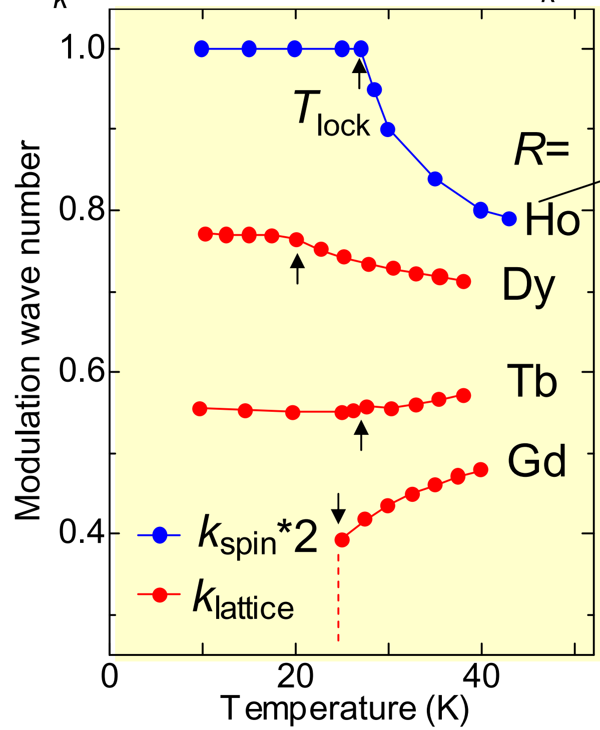


- $k_{\mathrm{lattice}} \doteqdot 2k_{\mathrm{spin}}$

Exchange striction $-J_{ij} S_i \cdot S_j$

Periodicity of modulation





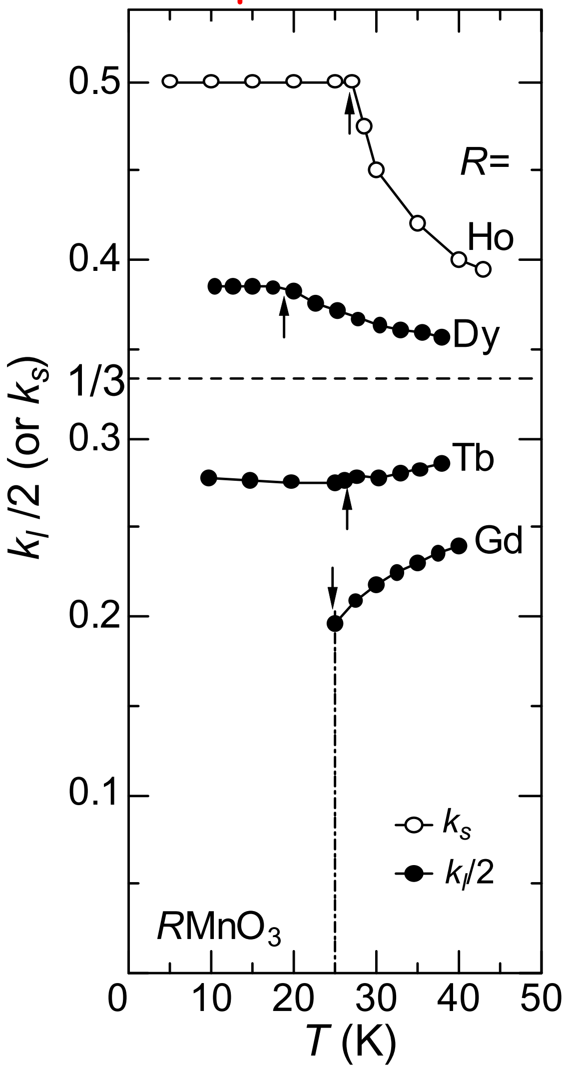
Munoz et al.
Inorg. Chem.
40, 1020 (2001)

Kimura et al.
PRB 68,
060403(R) (2003)

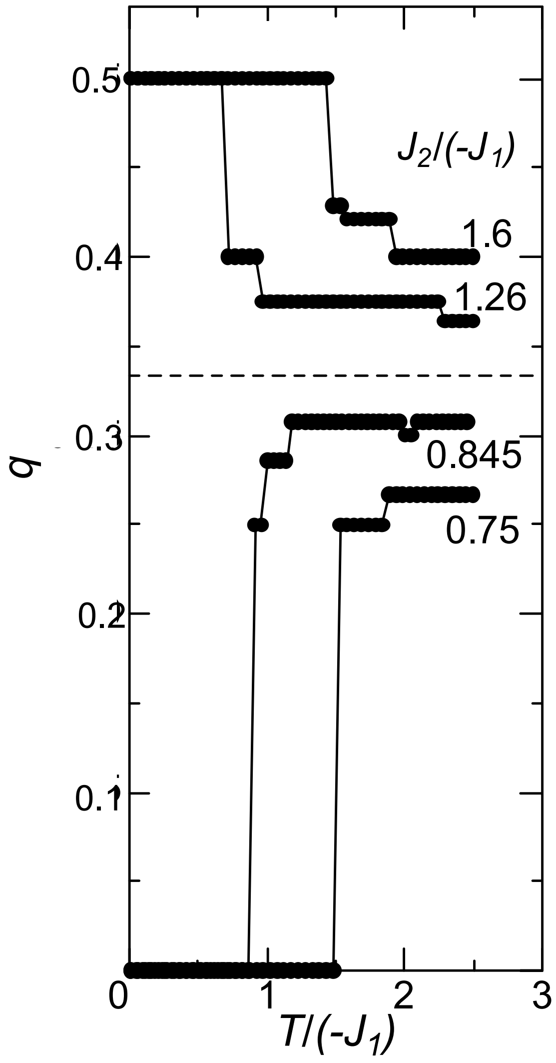
Modulation wave number along the *b*-axis of magnetic (k_s) or crystallographic (k_l) superstructure

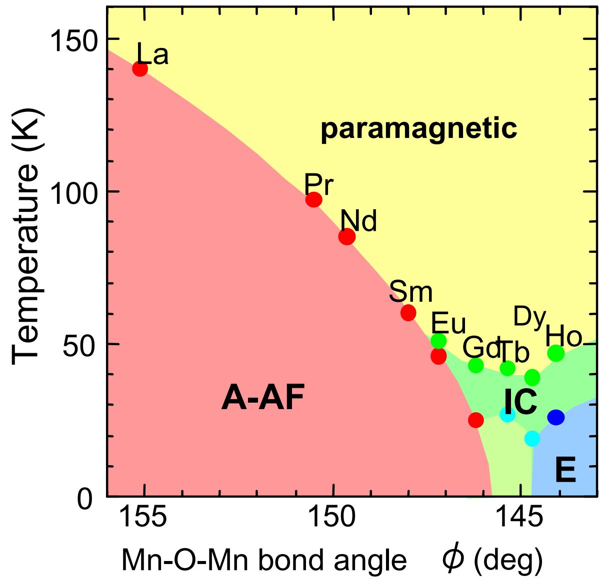
[data of $HoMnO_3$ taken from Munoz et al. Inorg. Chem. 40, 1020 (2001)]

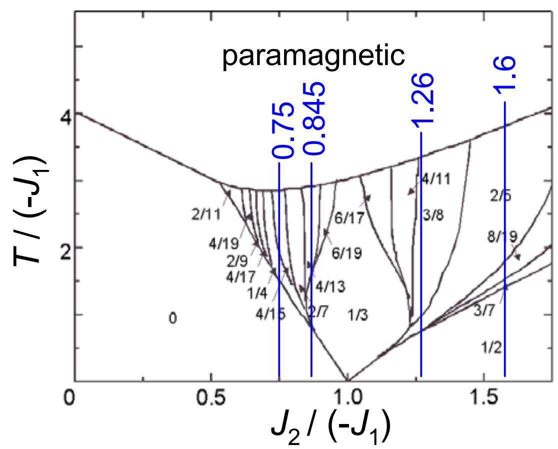
Experimental



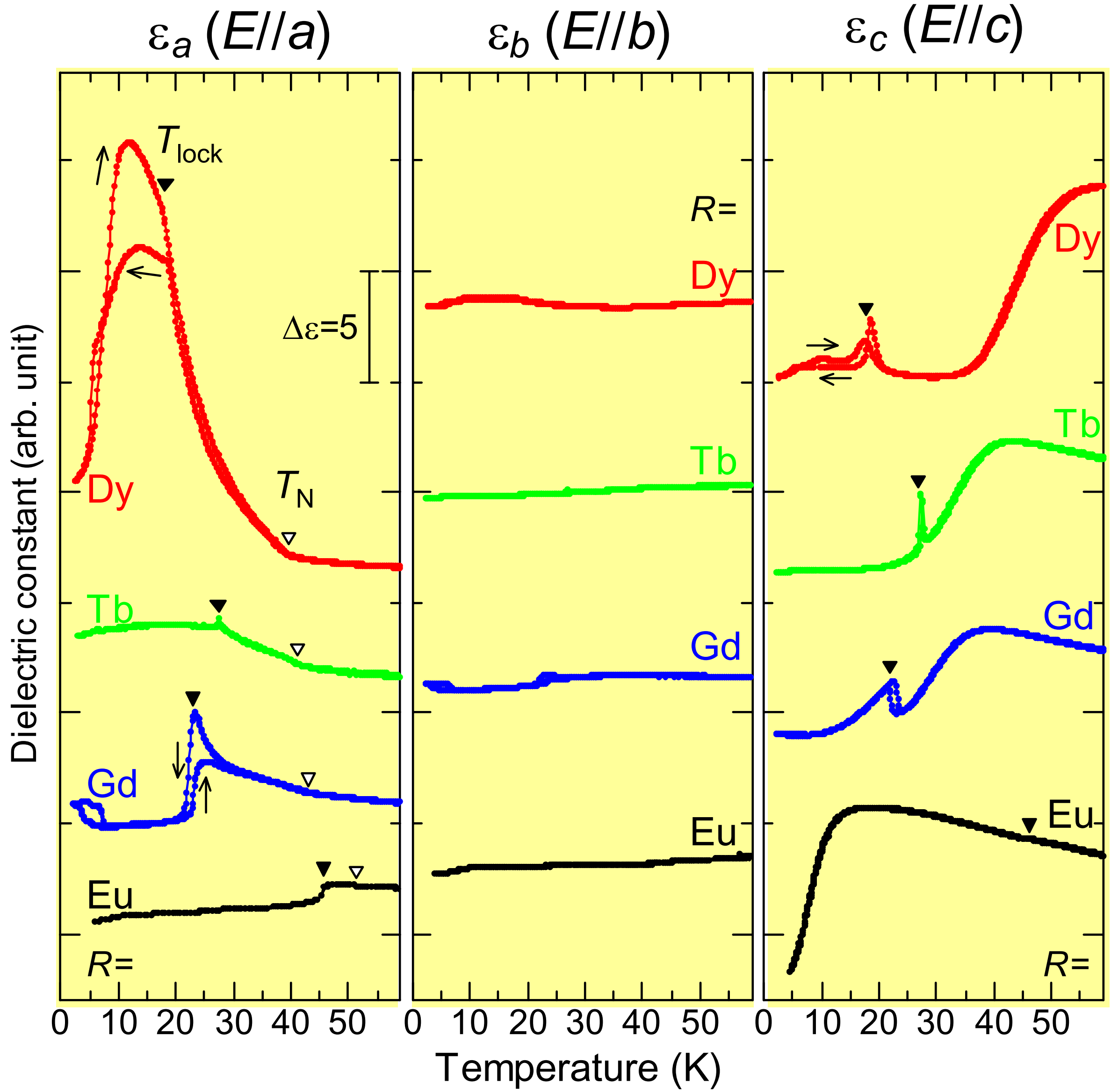
Calculation







Temperature profiles of dielectric constant in $RMnO_3$ (R = Eu, Gd, Tb, & Dy)

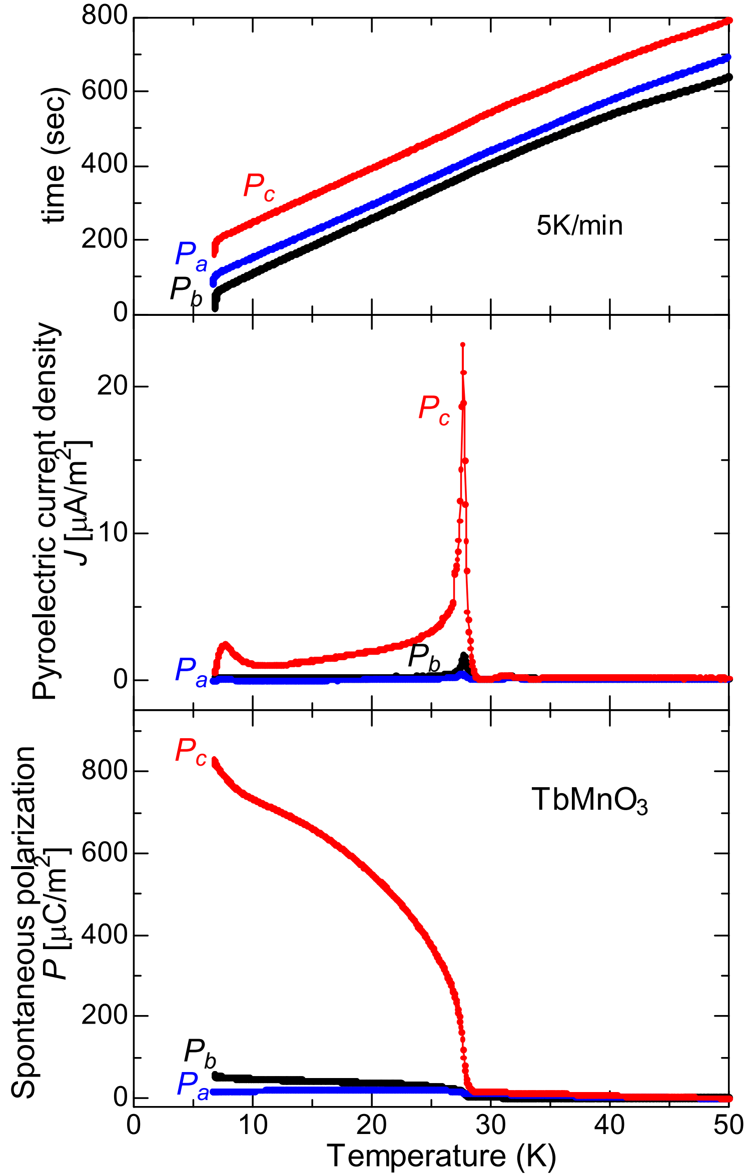


highly anisotropic

Dielectric anomalies at T_N & T_{lock}

Appearance of spontaneous polarization along the *c*-axis in $TbMnO_3$

- evidence of ferroelectricity -

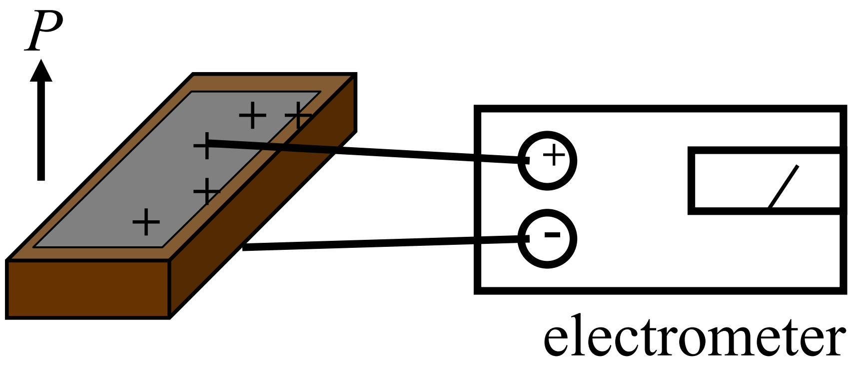


$$P = J\,t$$

P: electric polarization

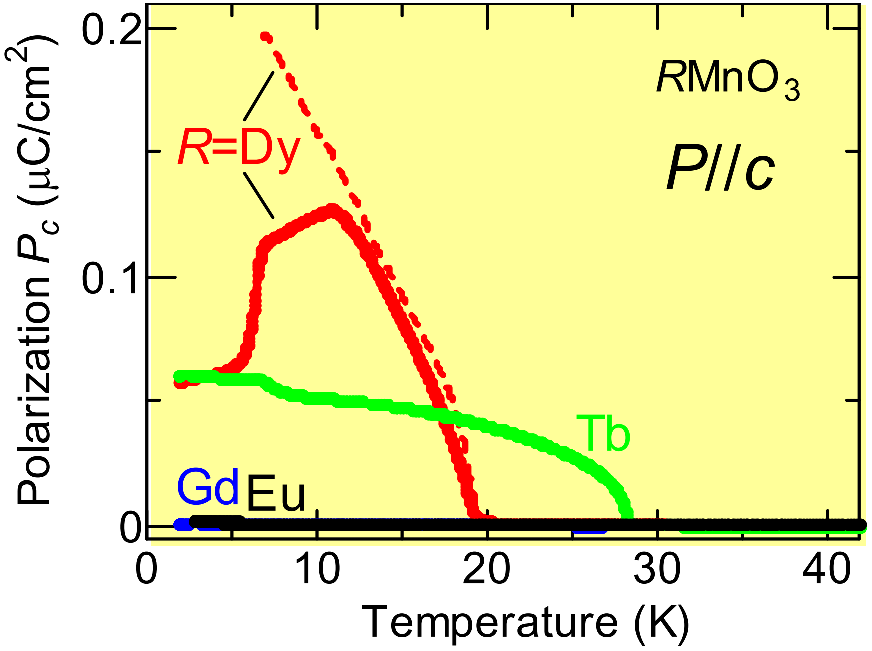
J: current density

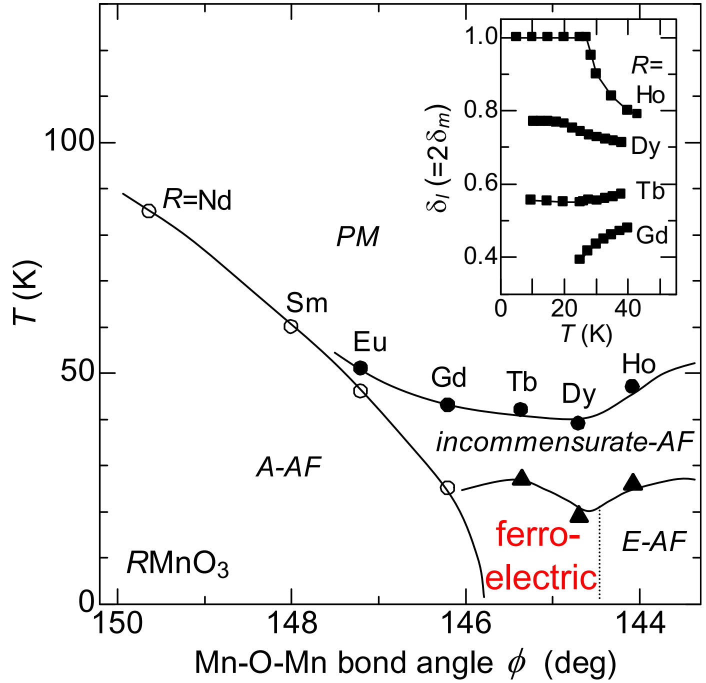
$$dP/dt = J$$



Temperature sweep

Temperature dependence of electric polarization along the c-axis in $RMnO_3$





c.f. $P_s(BaTiO_3)$ ~ 2.6×10^{-1} C/m^2 (296K)
$P_s(KNbO_3)$ ~ 3.78×10^{-2} C/m^2 (683K)

Spontaneous polarization appears along the c-axis below T_{lock} only in $TbMnO_3$ and $DyMnO_3$ having non-zero wave vector of lattice modulation.
[$k_l \neq 0$ in $(0,k_l,0)$]

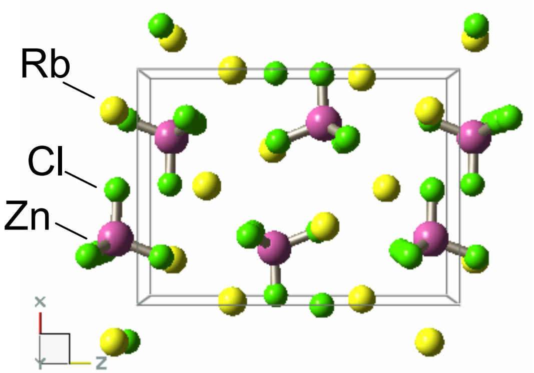
⇩

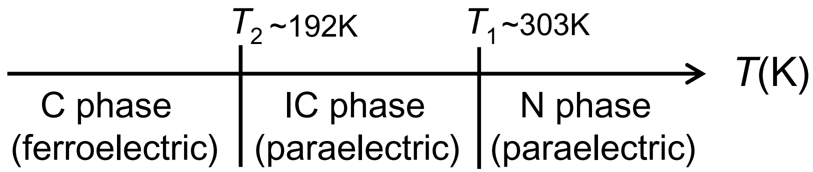
Improper ferroelectrics (e.g. K_2SeO_4, $RbZnCl_4$, etc.)

The primary order parameter represents the lattice distortion mode with a non-zero wave vector, and the spontaneous polarization appears as a secondary order parameter induced by the lattice distortion.

Improper ferroelectrics (e.g. Rb_2ZnCl_4)

Fundamental structure (N phase)
Pmca orthorhombic





At IC phase

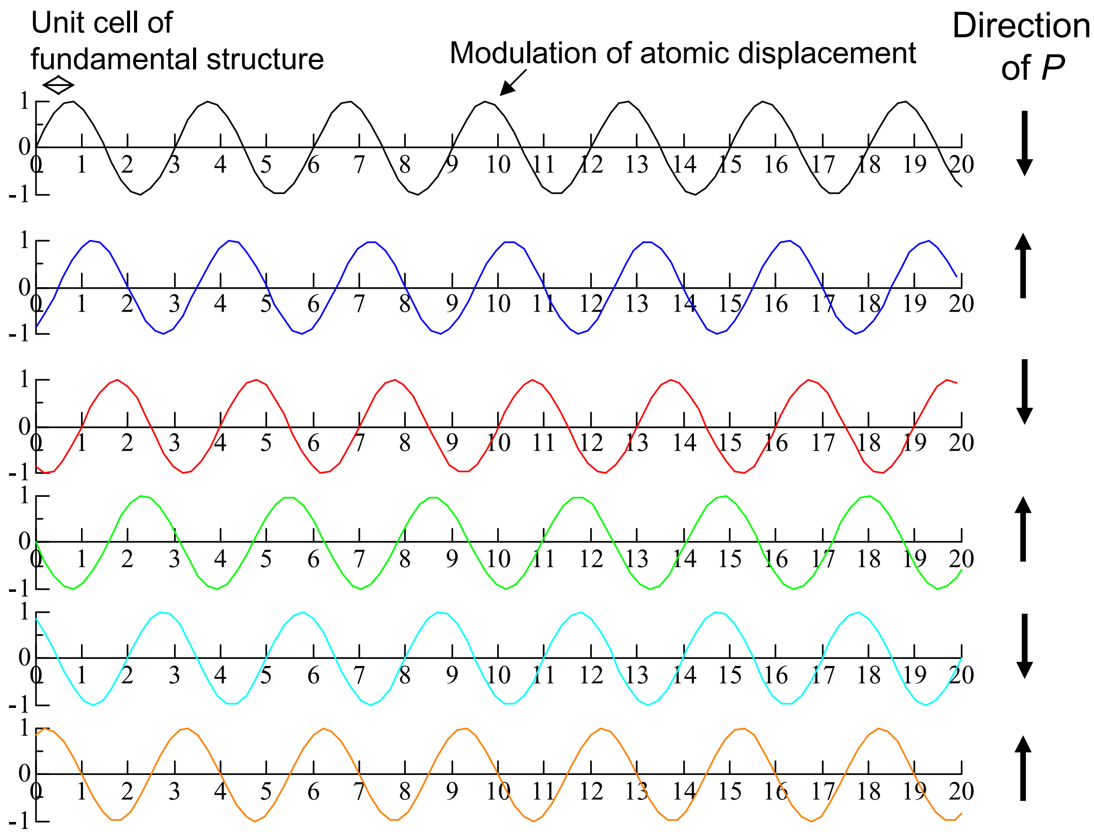
lattice modulation with
wave vector of $(1/3-\delta)c^*$

At C phase

wave vector of 1/3 c^*

$P2_1cn$ → ***P//a***

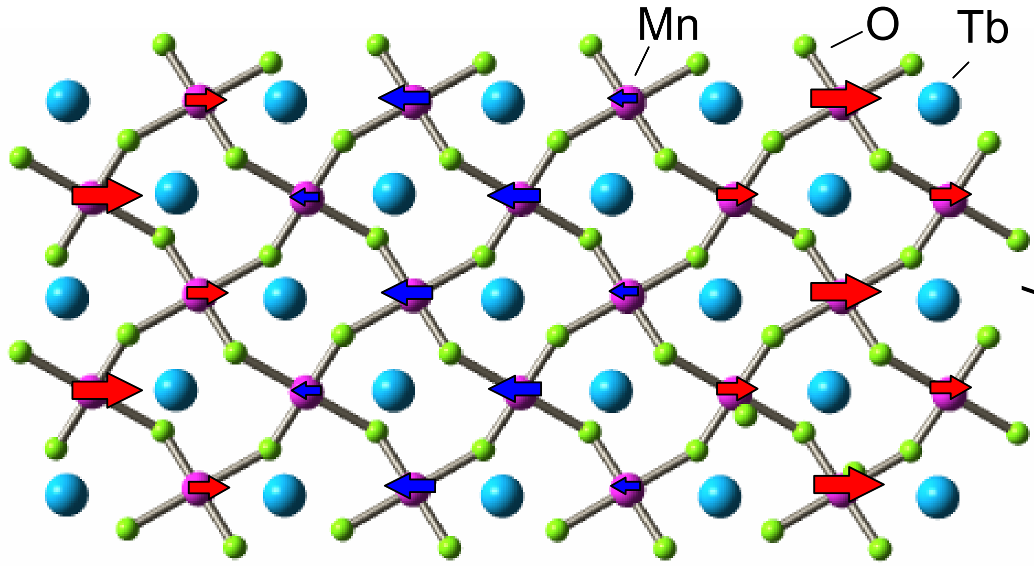
Phase of lattice modulation determines the direction of P at C phase

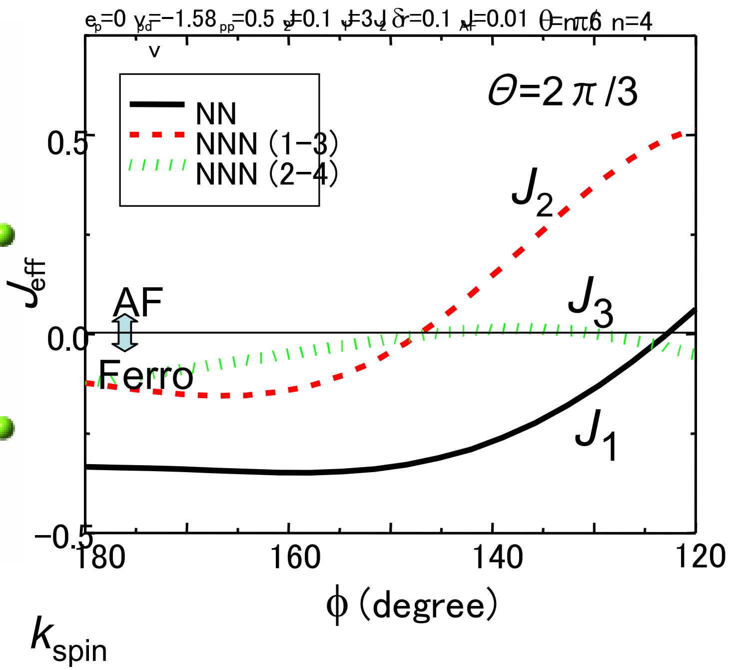


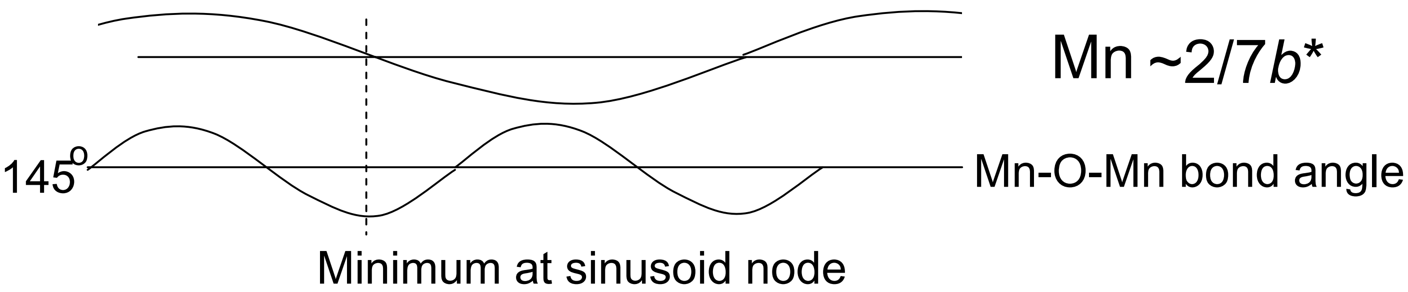
R. Blinkc & A.P. Levenyuk
Incommensurate phases in dielectrics
(North-Holland, Amsterdam, 1986)

Origin of lattice modulation and resulting ferroelectricity

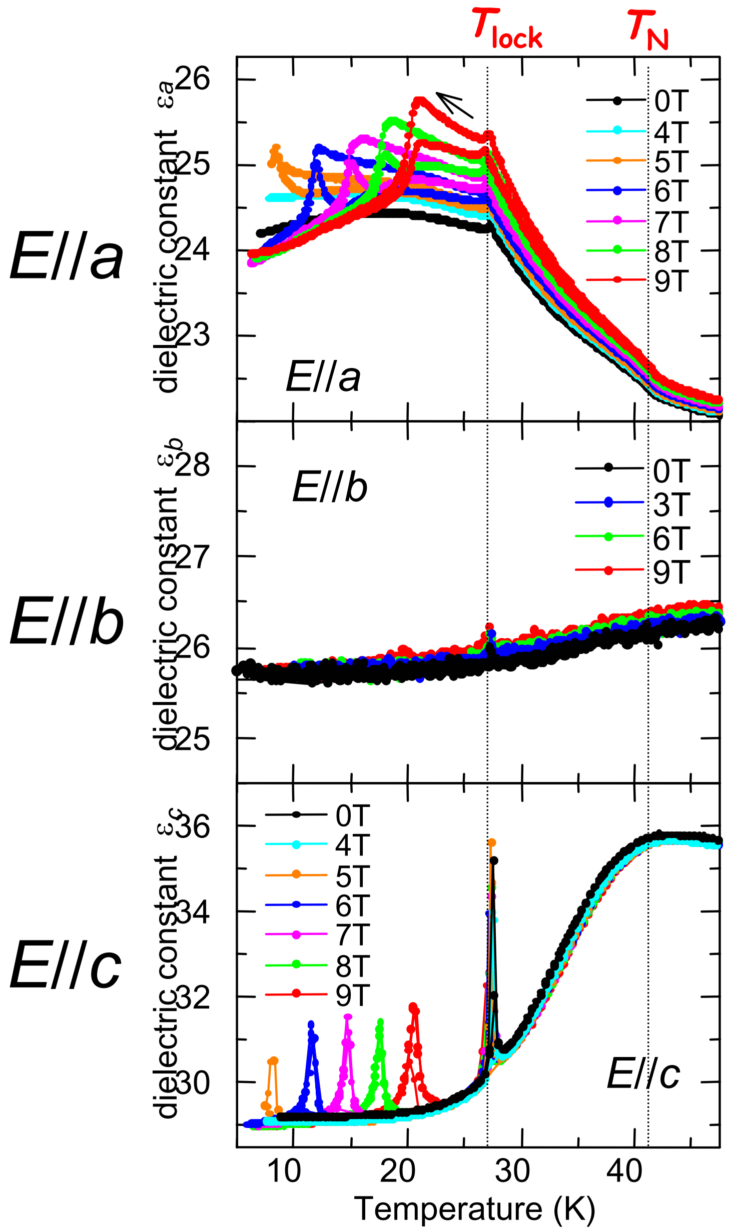
S. Quezel et al. Physica B 86-88, 916 (1977); R. Kajimoto et al. PRB 70, 012401 (2004)







Magnetic field effect on the dielectric constant (@10kHz) with *H//b* configuration



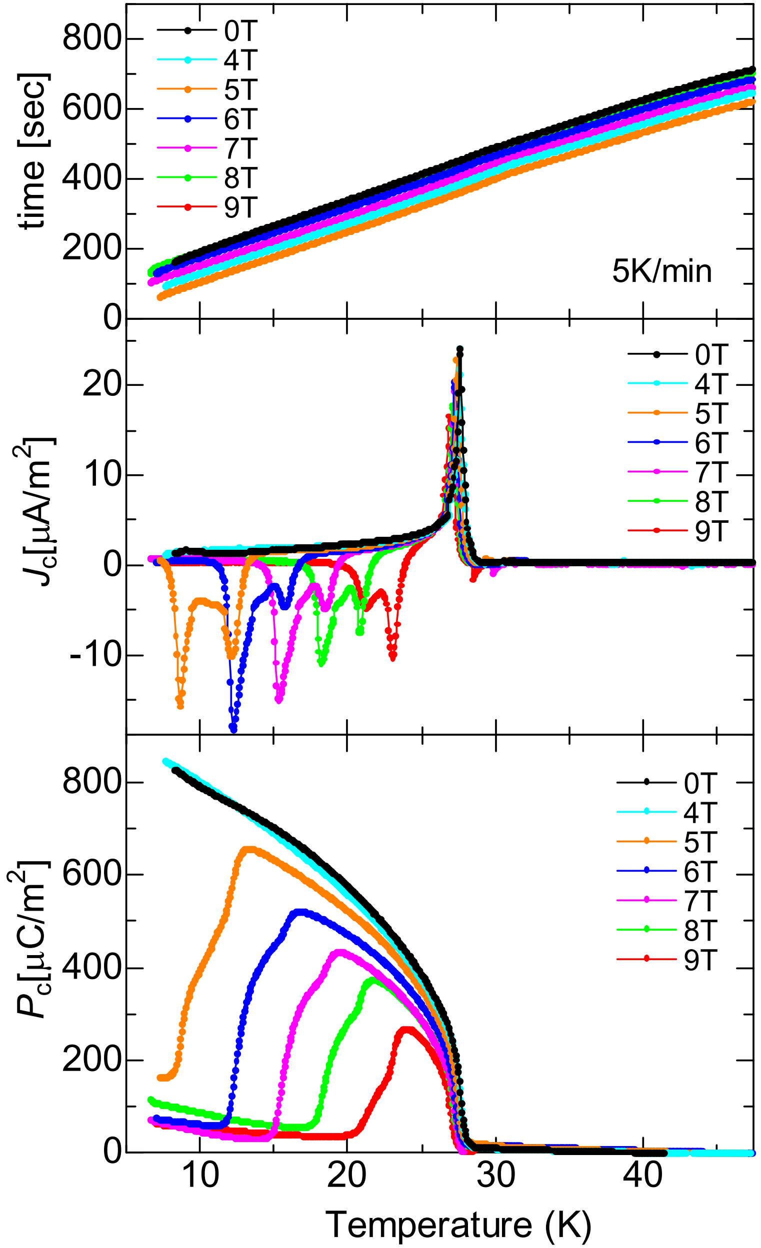
*Remarkable *H*-effect on ε_a & ε_c blow T_{lock}.

* T_{lock} is not shifted largely by magnetic field.

*Another peak structure in ε_a & ε_c appears by applying *H* above 5 T.

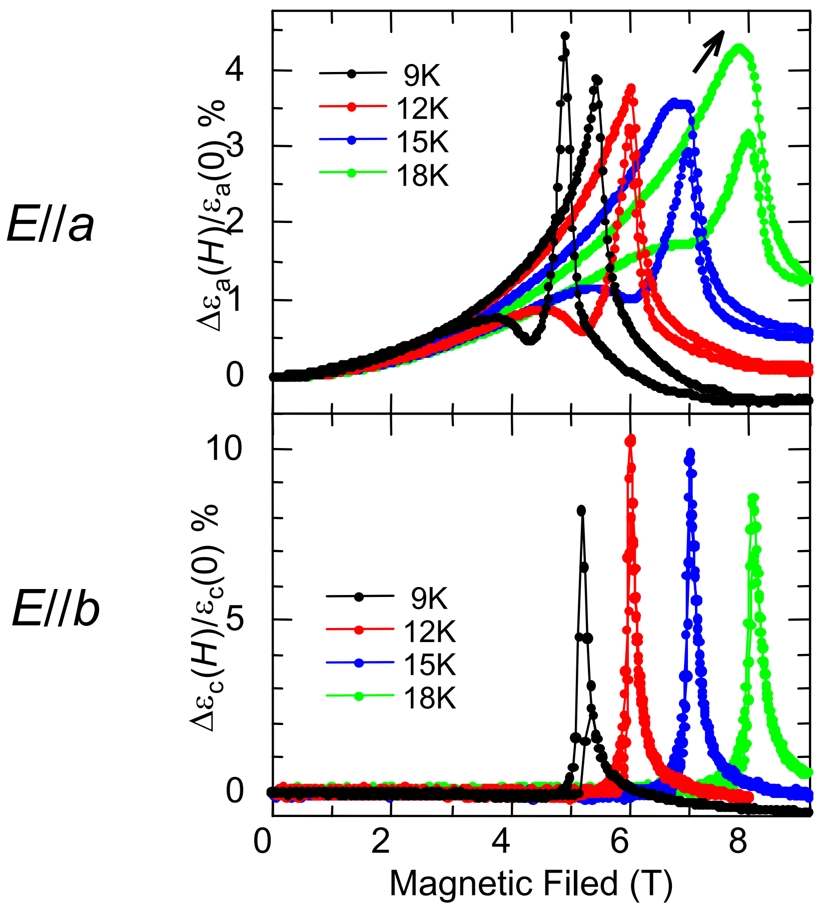
Magnetic field effect on pyroelectric current & spontaneous polarization in $TbMnO_3$

H//b, P//c



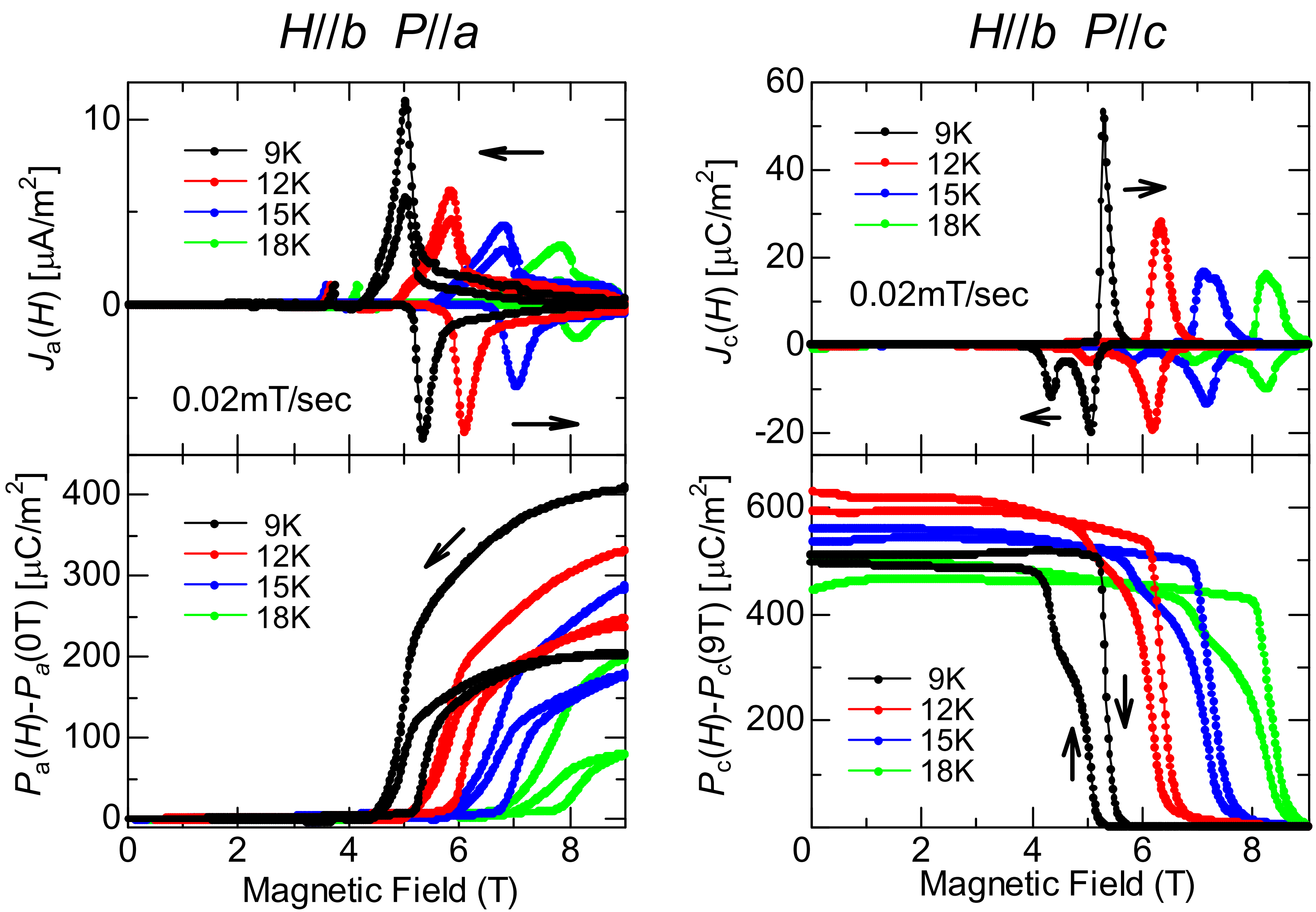
Giant Magneto-Capacitance effect in $TbMnO_3$ (*H//b*)

dielectric constant

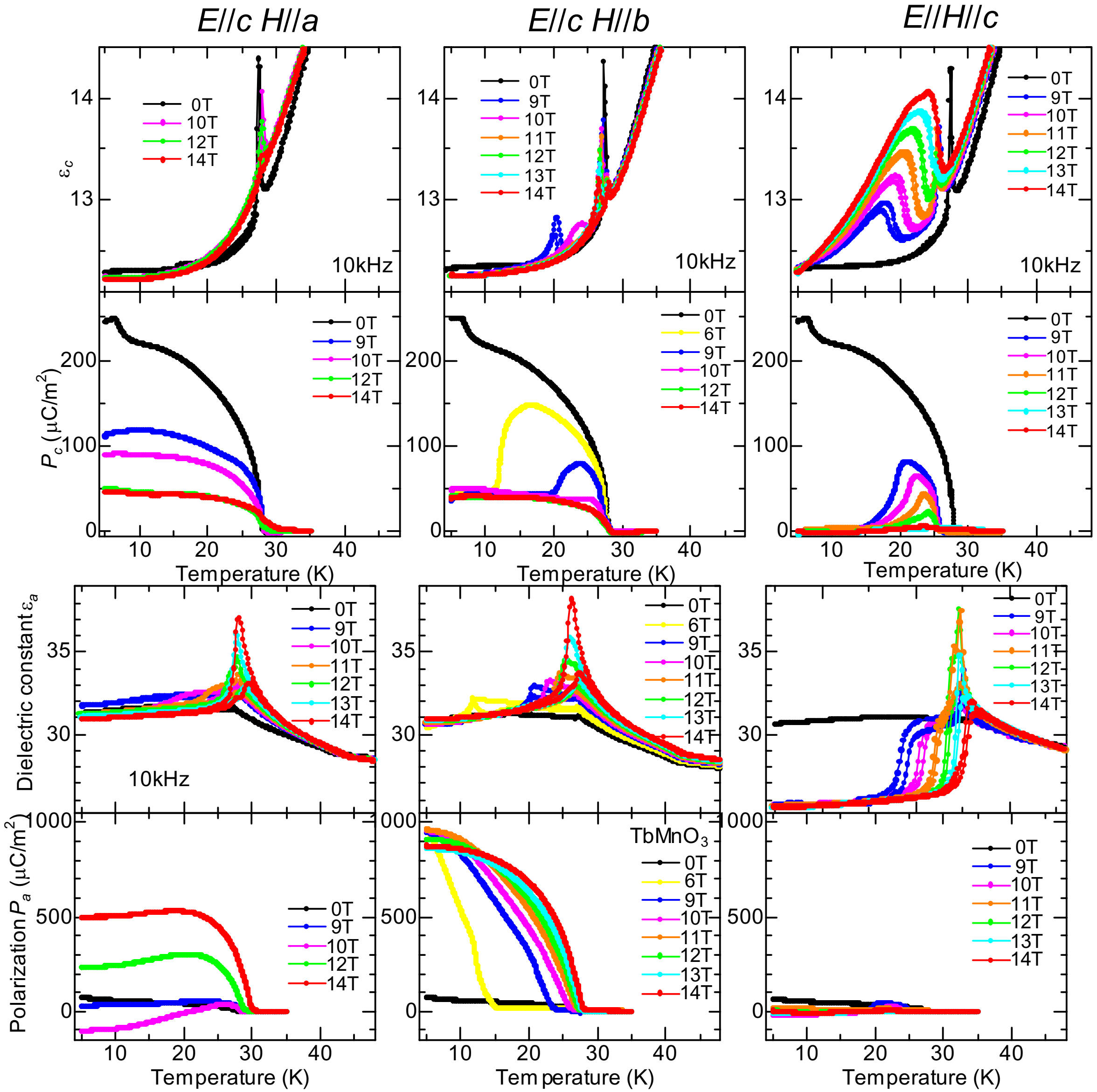


$\Delta\varepsilon(H)/\varepsilon(o)$ ~ >10%

Magneto-electric current & Magneto-electric effect in $TbMnO_3$



Dielectric constant & electric polarization of $TbMnO_3$ in high magnetic field

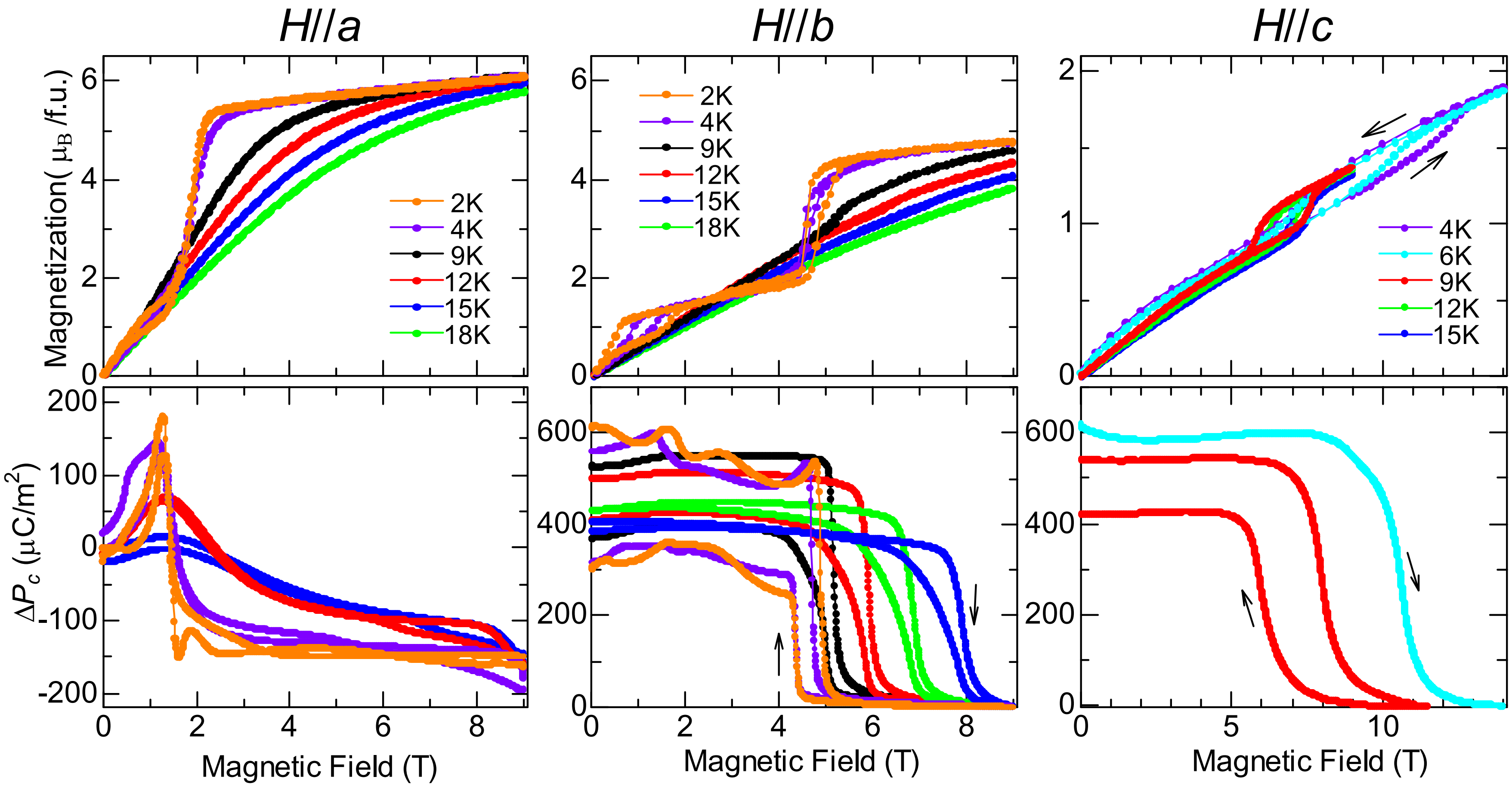


Direction of spontaneous polarization

	H=0T		H=14T
$H//a$	c	→	a
$H//b$	c	→	a
$H//c$	c	→	0

Strong coupling between magnetism & electricity -magnetic-field direction dependence-

$TbMnO_3$

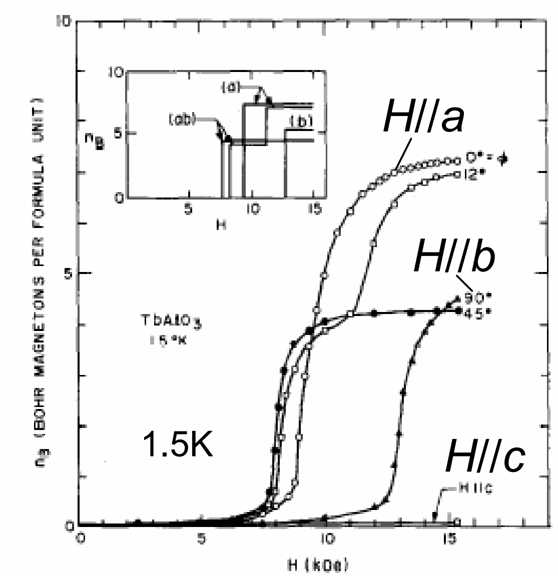


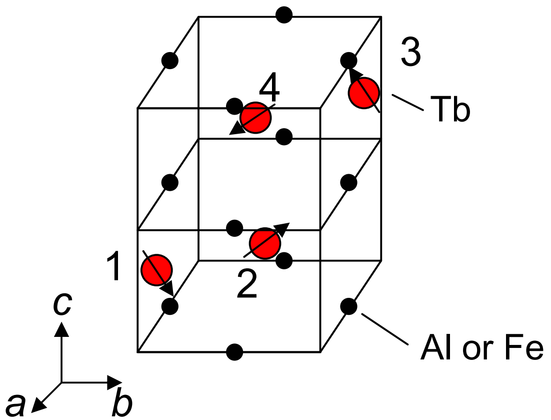
Metamagnetic transition causes change of electric polarization.

Metamagnetic transition in terbium perovskites

$TbAlO_3$

Home et al., JAP 39, 1373 (1968)

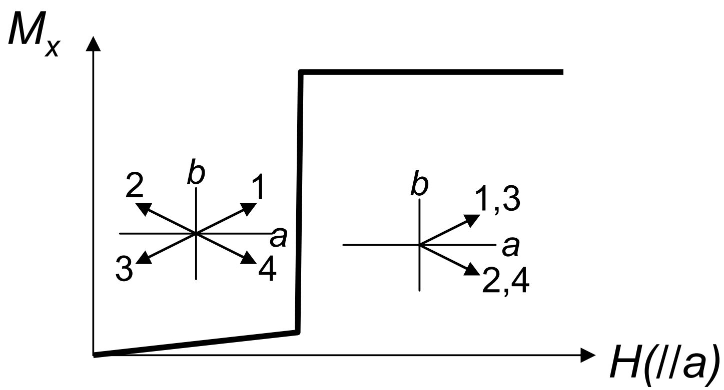


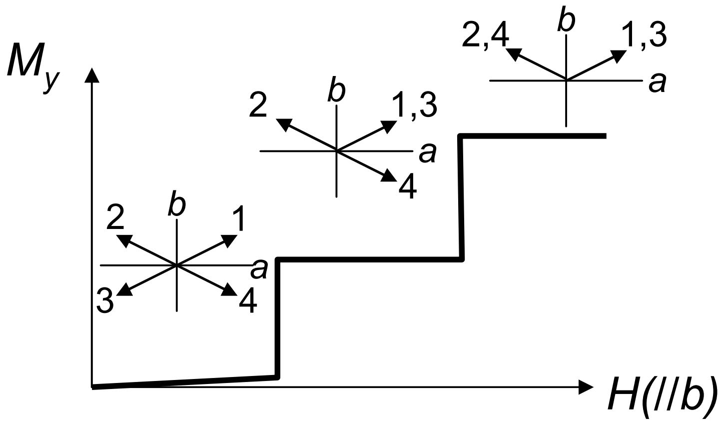


$TbFeO_3$

Bouree et al., J. de Phys. 36, 391 (1975)

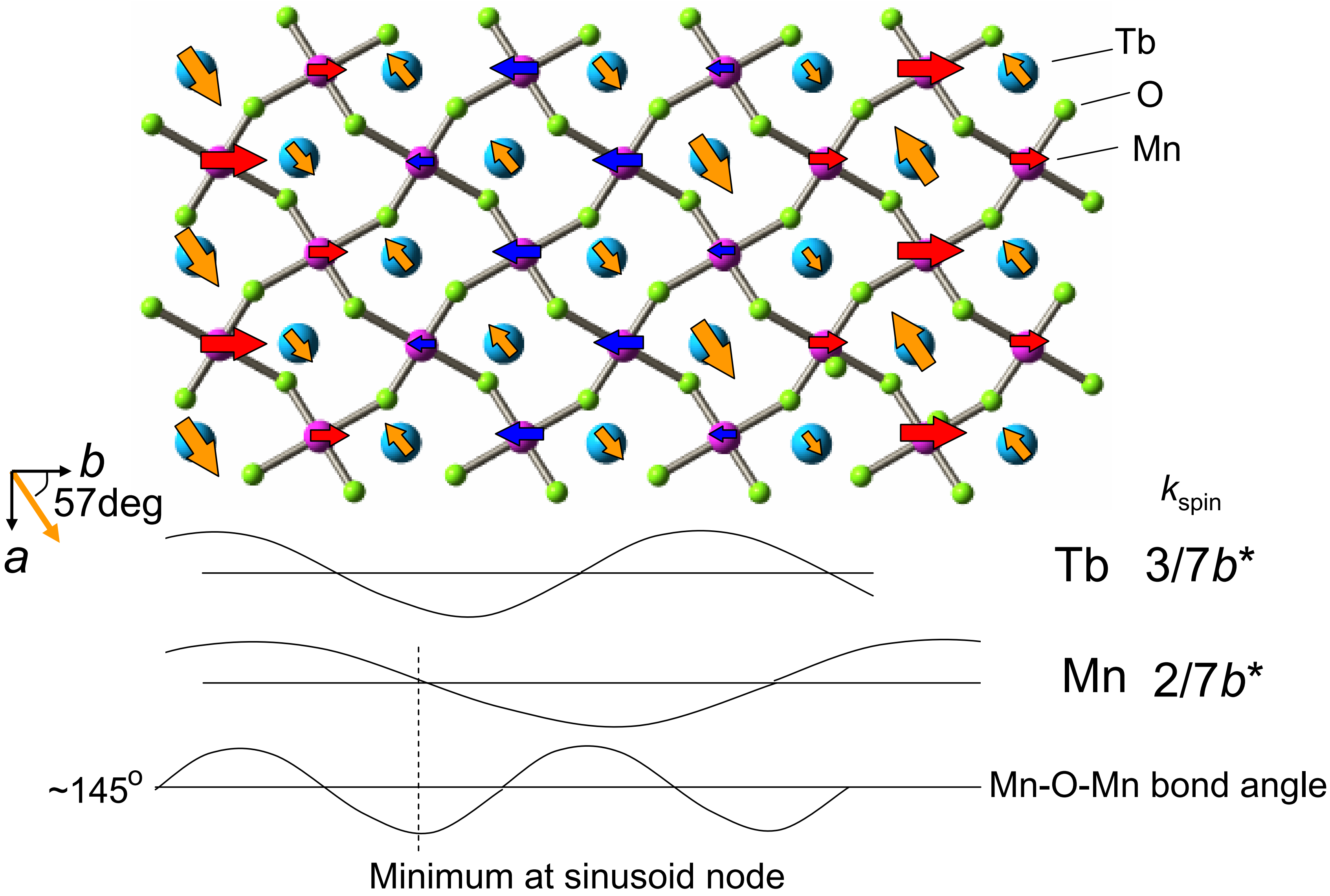
Belov et al., Sov. Phys. JETP 49, 723 (1979)





Schematic illustration of spin structure in $TbMnO_3$

S. Quezel et al. Physica B 86-88, 916 (1977); R. Kajimoto et al. cond-mat/0402439



Successive phase transition in betaine calcium chloride dihydrate (BCCD)

Unruh et al., SSC 70, 403 (1989)

Fundamental crystal structure; *Pbnm* orthorhombic

Existence of lattice modulation with the wave vector (0, 0, $\delta(T)$)

Devil's staircase

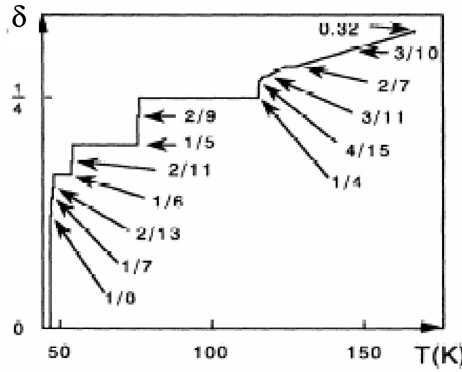


FIG. 1. Incomplete devil's staircase: the wave number $\alpha(T)$ for BCCD, labeling the phase sequence.

Commensurate phases of BCCD

$\delta = n/m$	*T*-range(K)	component of *P*
2/7	127-124	along *b*
3/11	118-117	0
1/4	115-76	along *a*
2/9	76-75	along *b*
1/5	75-53	0
	⋮	

Symmetry-based analysis can explain the variation of polarization accompanied by the change of δ.

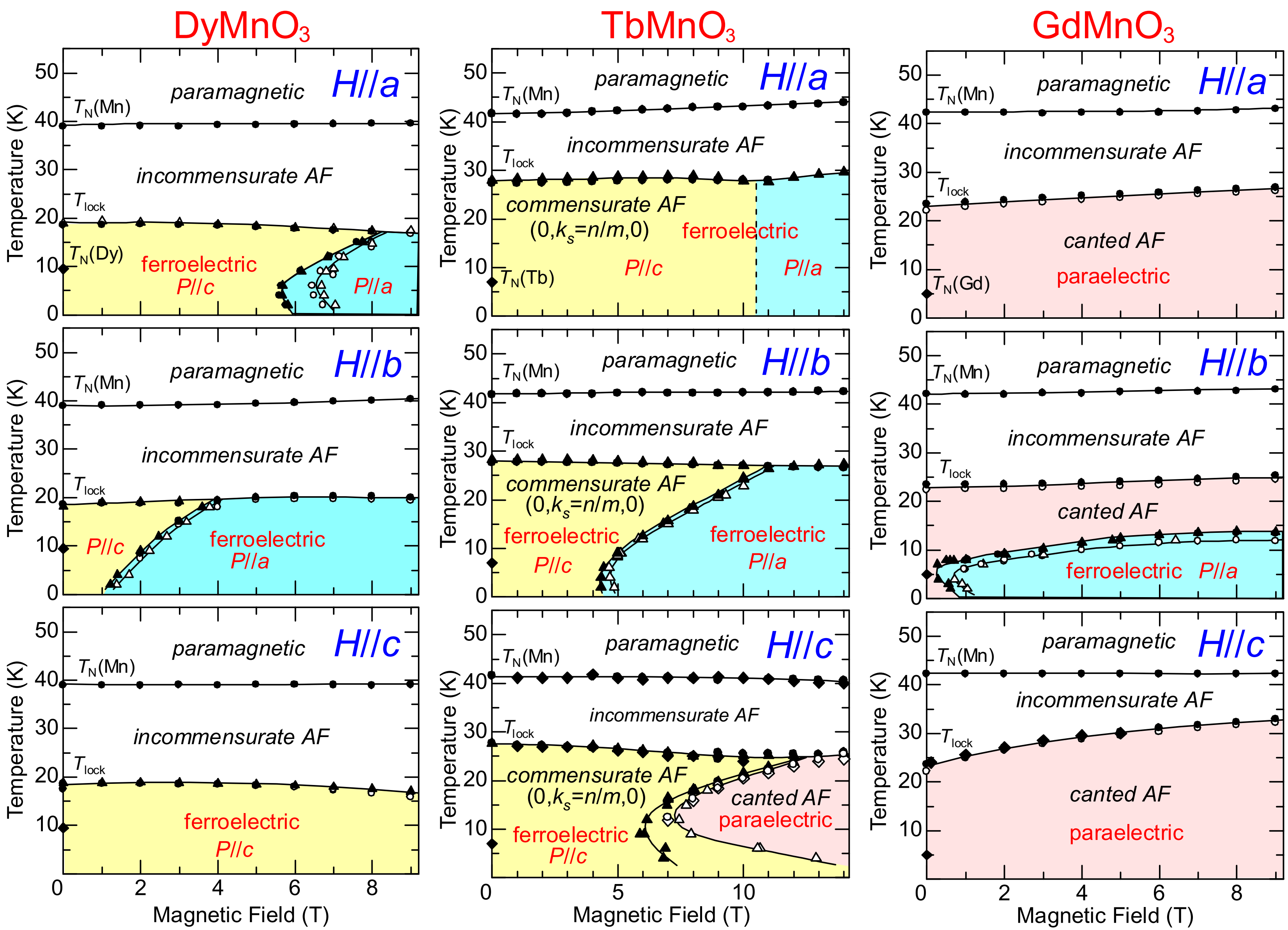
Perez-Mato, SSC 67, 1145 (1988).

⇩

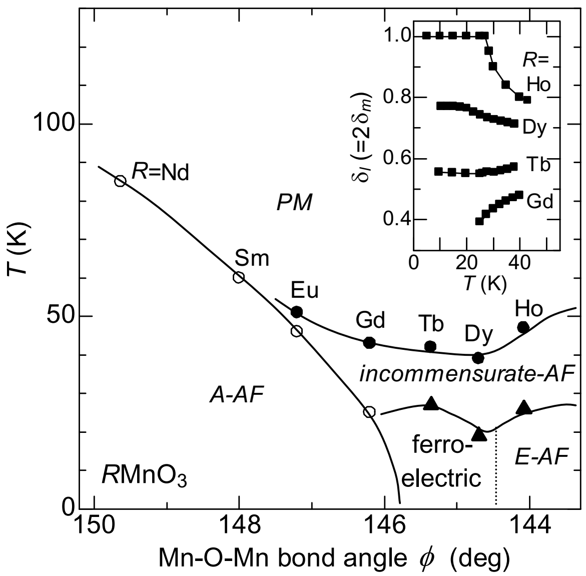
Polarity of modulated phase with $\delta = n/m$ depends on The parity of the function d and phase angle of the Modulation relative to the unit cell.

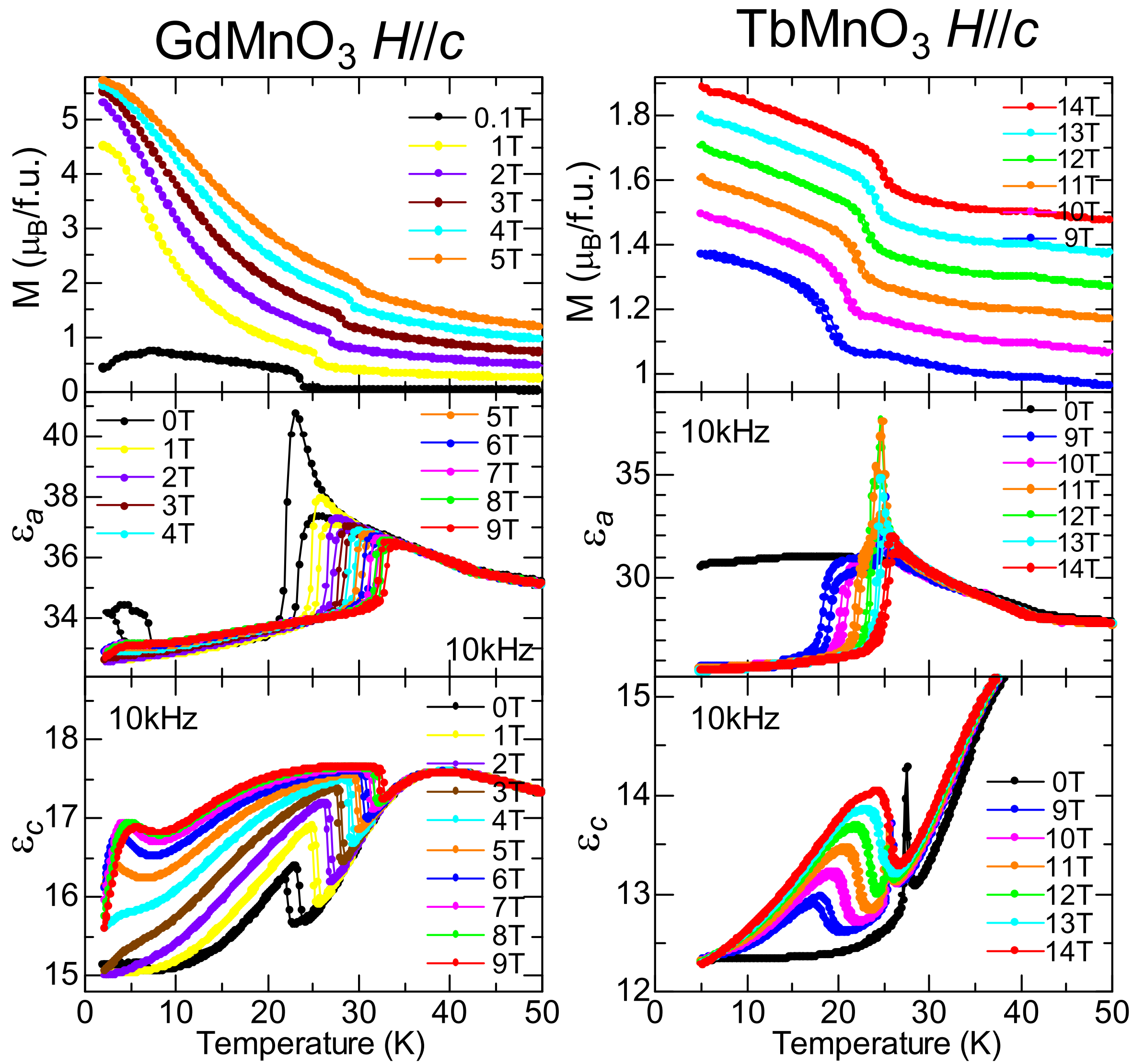
n/*m*	Label	ϕ	space group	*P*
odd/odd	I	0	$P112_1/a$	
	II	$\pi/2$	$P2_12_12_1$	
	III	arbitr.	$P112_1$	*z*
even/odd	I	0	$P2_1/n11$	
	II	$\pi/2$	$Pn2_1a$	*y*
	III	arbitr.	$Pn11$	*y*,*z*
odd/even	I	0	$P12_1/c1$	
	II	$n/2m^*\pi$	$P2_1ca$	*x*
	III	arbitr.	$P1c1$	*x*,*z*

Magnetoelectric phase diagram of RMnO$_3$ (R=Dy, Tb, & Gd)

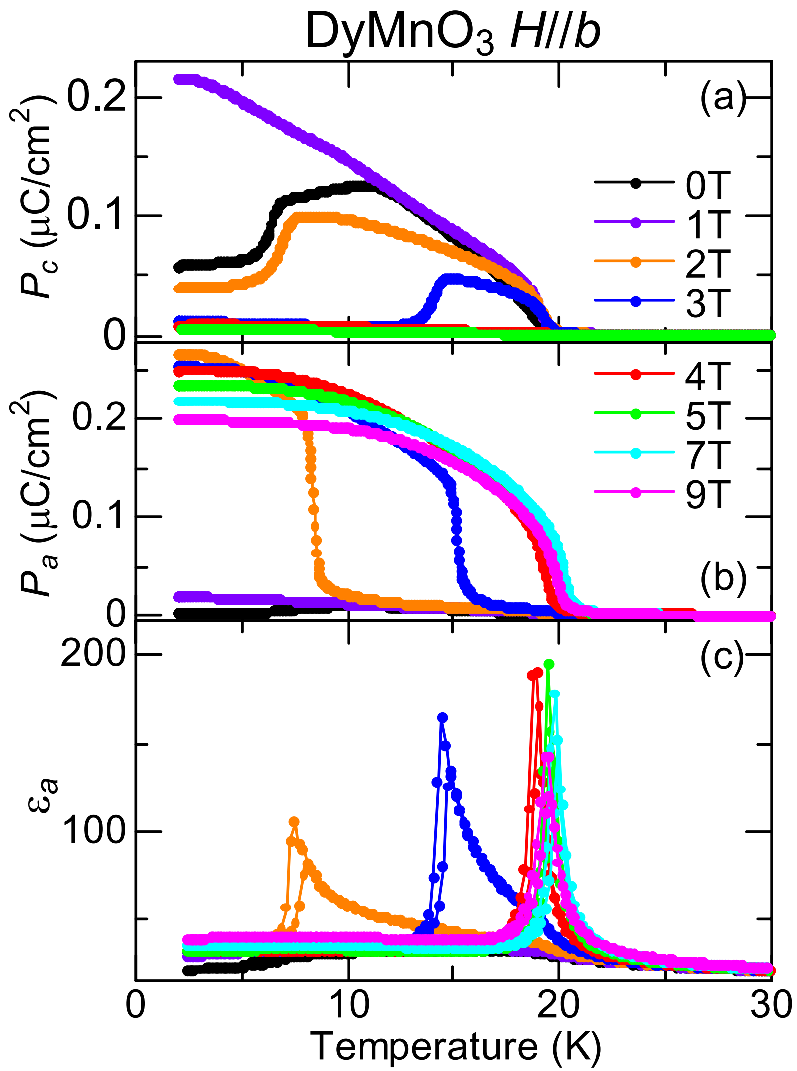


Similarity between $GdMnO_3$ (at low *H*) & $TbMnO_3$ (at high *H*)

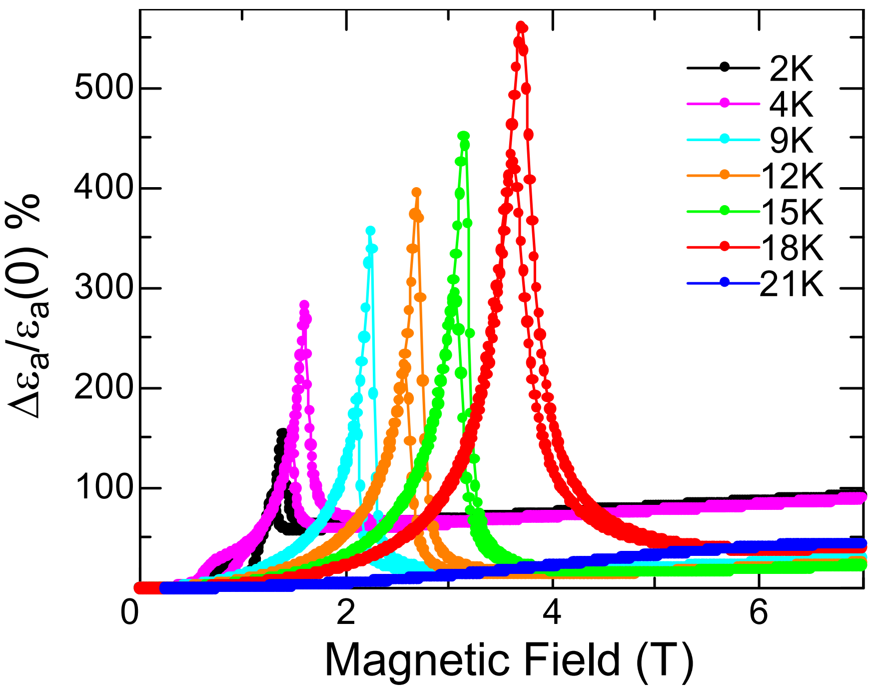




Giant magnetocapacitance effect in $DyMnO_3$



T. Goto et al., PRL 92, 257201 (2004)



Change of dielectric constant
by magnetic field exceeds ~500%

Summary

We found in perovskite rare-earth manganites $RMnO_3$

1. Incommensurate structural modulation accompanied by sinusoidal spin order $k_{lattice} = 2 * k_{spin}$

2. Ferroelectricity below lock-in transition

3. Magnitude and direction of electric polarization can be tuned by magnetic field, which gives rise to gigantic magnetocapacitance and magnetoelectric effects

The observations will provide new aspect of the research for spin systems with competing magnetic interactions.